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Digest of
Report K-1649

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
Fiscal Year 1964 through Fiscal Year 1965

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Technical Division
Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
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Oak Ridge, Tennessee

Report Date: October 29, 1965 Report Classification: Unclassified

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Basic technology for recovering both high and low enrichment fuels by volatility methods is being provided by the Argonne, Oak Ridge, and Brookhaven National Laboratories. During the past two years, the Oak Ridge Gaseous Diffusion Plant Technical Division has supported the main effort of the National Laboratories in two ways. First, conceptual plant studies have been performed, including economic comparisons of alternative process flow sheets. These evaluations have attempted to define process problem areas and to point to the optimum route to a successful commercial enterprise. Second, a components development program has been initiated covering scale-up and testing of crucial process equipment and auxiliaries. This report is primarily a summary presentation of the Oak Ridge Gaseous Diffusion Plant work carried out during fiscal years 1964 and 1965.

The report is 112 pages long and contains 39 figures and 18 tables.

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ABSTRACT

During the past several years, the Atomic Energy Commission has been sponsoring technical and scientific studies of a group of processes aimed at recovering valuable uranium and plutonium from spent nuclear reactor fuels by dry gas techniques. In essence, these elements are volatilized as the hexafluorides, and most of the undesirable fission products are left behind. Purification from volatile fission products is accomplished by distillation or selective sorption.

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ORGDP FUEL REPROCESSING STUDIES
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INTRODUCTION

Competitive nuclear power depends upon the realization of certain technological and economic successes, and an important part of the overall picture is the fuel cycle. With the development and demonstration of economically sound systems for reprocessing nuclear fuels as its stated objective, the AEC's Chemical Separations and Development Branch has supported comprehensive development programs at the Argonne, Oak Ridge, and Brookhaven National Laboratories.

The design of the first commercial reprocessing plant to be built, i.e., Nuclear Fuel Services, was based on the aqueous separations technology which had a history of use at government plants at Hanford, Savannah River, and Idaho Falls and major long-term technical support from ORNL, ANL, and BNL, as well as from the processing sites themselves. During the past several years, the AEC has also been sponsoring technical and scientific studies of a basically different group of processes aimed at recovering valuable uranium and plutonium by dry gas techniques. In essence, these nuclear fuels are volatilized as the hexafluorides, and most undesirable fission products are left behind. Purification from volatile fission products is accomplished by distillation or selective sorption.

Basic technology for recovering both high and low enrichment fuels by volatility methods has been and is being provided by the three National Laboratories already named. Particularly, at this writing, participating groups are fully occupied exploring the chemical and technical feasibility of the various process alternatives for handling low enrichment fuels. Laboratory development programs on high enrichment fuels are essentially complete.

During the past two years, the Oak Ridge Gaseous Diffusion Plant Technical Division has supported the main effort of the National Laboratories in two ways. First, conceptual plant studies have been performed, including economic comparisons of alternative volatility process flow sheets. These evaluations have attempted to define process problem areas and to point to the optimum route to a successful commercial enterprise. Second, a components development program has been initiated covering scale-up and testing of crucial process equipment and auxiliaries. In some cases, e.g., the process recycle compressor, the complete development and design program has been undertaken at the ORGDP.

The report which follows is primarily a summary presentation of the work carried out during fiscal years 1964 and 1965. Bimonthly progress reports have been issued regularly during this period to a limited AEC distribution. Henceforth, ORGDP work will continue to be reported bimonthly and summarized semiannually.

SUMMARY

ENGINEERING STUDIES

Studies of the economic and technical feasibility of processes for r
covery of fissile material from irradiated nuclear fuels are being p
formed at the Oak Ridge Gaseous Diffusion Plant to provide guidance
the associated laboratory and engineering experimental programs supp
by the Chemical Separations and Development Branch of the Division o
Reactor Development. The tangible result of such evaluations is the
velopment of conceptual plant designs with associated costs accompar
by realistic appraisals of potential scale-up problems. Coupled wit
this engineering effort is a comprehensive systems analysis study de
to summarize the large number of process alternatives and problems a
to indicate those work areas that should be emphasized in the integ
overall DRD program.

A brief resume of ORGDP feasibility studies (both completed and in p
gress) concerned with reprocessing of spent high enrichment uranium
and power reactor clad uranium dioxide materials appears in this rep
Included also are more detailed calculations relating to specific p
lems, such as alumina bed usage economics, bed temperature rises due
radioactively generated heat, criticality considerations for high an
low uranium enrichment fuels, and cold trapping equipment.

Historically, the ORGDP participation began with the evaluation of p
cesses for high enrichment fuels, since National Laboratory develop
programs were considerably more advanced for this class of fuel. Th
emphasis has now shifted almost completely to the low enrichment pow
reactor fuels; however, much of the component work and, to a lesser
tent, the engineering analyses is applicable to either high or low
richment materials.

HIGH ENRICHMENT FUELS

Survey analyses were first made for classified fuel flow sheets, in
ing both different volatility process approaches and comparison aqu
routes. These engineering evaluations of technology and economics
used for program planning purposes. The major conclusions were tha
tility processes were at least competitive with aqueous routes and
the fluid-bed volatility approach coupled more versatility than the
competitor, molten salt processing, with a high probability of ulti
success. Additionally, fluid-bed processes were deemed to be more
able to power reactor fuel treatment, including plutonium recovery.

Accordingly, it was requested by the AEC that a definitive evaluati
covering aluminum, zirconium, and graphite-base fuels and using the
estimates of generation rate be performed for a fluid-bed volatilit
This study is now in progress.

LOW ENRICHMENT POWER REACTOR FUELS

The present volatility program emphasis is on developing processes for recovery of uranium and plutonium by volatilization as the corresponding hexafluorides from low enrichment zircaloy and stainless steel-clad fuels. Since it appears that the zircaloy-clad fuels may predominate in the future, the initial study is aimed at these materials.

Many decisions regarding basic technology application still remain to be made, as well as others involving more strictly economic optimization. The discussion in the body of this report covers selected alternative process routes which may be considered reference flow sheets, since they have been accepted by the participating groups as such.

Zircaloy-Clad Fuel Process

The present flow sheet for zircaloy-clad fuel calls for removal of the clad by volatilization with hydrogen chloride gas at about 400°C. The reaction with the fuel charge takes place in a head end reactor containing a fluid bed of alumina grain. Pyrohydrolysis at 350°C. is used in a second fluid bed to convert the zirconium and tin compounds to the oxide form for storage as solids. Although the oxide fuel fragments will be relatively unattacked by the hydrogen chloride, some radioactive material will be volatilized during the hydrochlorination; however, except for the noble gases, these substances are expected to be retained in the hydrolysis reactor bed. The uranium oxide fuel fragments remaining in the head end fluid bed are oxidized to a fine powder at about 400°C., and the resulting uranium and plutonium oxides are fluorinated using elemental fluorine at temperatures graded from 400 to 550°C. Since most of the elements comprising the bulk of the fission product activity and transuranic elements (except neptunium and plutonium) form nonvolatile fluorides which remain in the fluid bed, considerable decontamination of the uranium and plutonium is achieved by the volatilization as the hexafluorides. Plutonium tetrafluoride is produced by thermal decomposition of the plutonium hexafluoride in the absence of fluorine. The uranium hexafluoride is then purified of remaining fission products and traces of plutonium and neptunium by distillation and sorption on magnesium fluoride and hot sodium fluoride.

Although much basic information remains to be developed with regard to this flow sheet sequence, ANL work to date has given a degree of confidence that plutonium can indeed be volatilized and transferred. The uranium recovery aspect certainly appears technically feasible; however, additional scale-up work is required.

Stainless Steel-Clad Fuel Process

The present preferred process for stainless steel-clad uranium dioxide fuels utilizes a hydrogen fluoride-oxygen gas at 600°C. to spall off the cladding in rusty fragments. The uranium dioxide pellets are concurrently broken up into fine powder and are converted to uranyl fluoride and uranium tetrafluoride.

The uranium and plutonium recovery and purification aspects of stainless steel-clad fuel reprocessing would be about the same as for the zircaloy materials.

Interhalogen Flow Sheet

Flow sheets employing bromine pentafluoride for removal of the uranium are now being evaluated. Uranium salts can be readily converted to uranium hexafluoride with this reagent, while for thermodynamic reasons, plutonium hexafluoride should not be formed. Thus, a clean separation of uranium and plutonium in the fluid-bed fluorinator should be possible, and simplifications in the product handling system may be achievable.

Several flow sheets involving different arrangements of the bromine halide recycle and uranium hexafluoride purification equipment are being considered.

Head End Fluid-Bed Reactor

A two-diameter fluid-bed reactor is contemplated for the conceptual plant unit. The lower section would be of small diameter to allow attainment of higher gas velocities for improvement of heat transfer and powder carryout during the oxidation of pellet fragments and reaction of other fuel constituent pieces. The larger, upper diameter permits insertion of the fuel charge and sufficient reduction of exit gas velocities to prevent excessive elutriation.

Radioactive Heat Generation

Radioactive heat generation poses a problem in (a) fuel charging machinery, (b) the fluid bed in removal of heat from newly charged elements should fluidization fail, and (c) the contaminated bed solids if bed caking or settling occurs. Calculations made for various possibilities indicate that temperature rise at the bed centerline can be generally assumed to be adiabatic for the contemplated plant reactor size.

One conclusion from the calculations is that temperature rise rates are large enough to impose significant problems, particularly with short cooled, high burnup material. Temperature rise rates on the order of 50 to 100°C. per hour may be typical. Obviously, this is not a serious problem in the same way that a nuclear reactor transient hot spot might be; however, it would require corrective action to "unstick" the bed in a fairly short time, in chemical plant operating terms.

Alumina Diluent and Bed Storage Costs for Power Reactor Fuel Processing

Calculations have been made relating to the economics of bed recycling, including alumina cost, fuel cooling time before processing, and waste storage investment, using bin storage costs developed at the Idaho Chemical Processing Plant. Ultimately, waste disposal might require different hardware; however, storage in bins appears most reasonable at present. The conclusion is that waste storage capital costs are of the same order of magnitude as the value of plutonium losses of 1%.

There is a sizable incentive from both waste storage and plutonium loss economic viewpoints of holding the ratio of diluent alumina used to uranium throughput as low as possible. Presently, the target value for this ratio is 0.4.

CRITICALITY CALCULATIONS

High Enrichment Fuels

Criticality calculations are presented for highly enriched uranium. Considerable operational advantage is derived from elimination of hydrogeneous moderation from the process system, and the minimum critical mass for a uranium density of 3.2 g./cc. or less appears to be in excess of 109 kg.

Low Enrichment Fuels

Critical mass calculations for uranium dioxide pellet charges for dry systems and in the presence of liquid water are presented for uranium-235 assays of 2 and 5%. According to the calculations, dry systems are inherently safe for these enrichments, since the infinite medium neutron multiplication constants are less than 1. With liquid water present, however, criticality could be achieved with masses substantially less than those proposed for batch charges. Precautions in design, such as avoidance of water cooling for the reactor and use of temperature interlocks, will essentially eliminate the possibility of water accumulation in the equipment.

Plutonium

Critical mass calculations were made for plutonium oxide spheres reflected with alumina to provide orientation for problems involved in power reactor fuel reprocessing. At a plutonium density of 4.6 g./cc. with a 50 cm. alumina reflector and assuming all plutonium is as the 239 isotope, the critical radius was indicated to be 10.79 cm. with a corresponding critical mass of 24.2 kg. of plutonium.

COLD TRAPS

Batch desublimers (cold traps) are used to collect uranium hexafluoride from gas streams. To aid in the design of such units, a desublimer design digital computer program is being developed. Preliminary computer results agree well with available experimental data.

PROTOTYPE TESTING AND EVALUATION

Development work is proceeding in a number of areas where additional information is required for design of a production facility. Of primary importance is extension of the Argonne National Laboratory, Oak Ridge National Laboratory, and Brookhaven National Laboratory work on volatility processes by studies in larger equipment. In some cases, scale-up from relatively small experimental equipment may be possible; in

others, tests in up to half or even full size reactors will be required. Also of major importance are materials of construction, outlet gas filters, product purification systems, remotely operable connectors, gas compressors, cold traps, and reactor fabrication procedures. As the work progresses, need for investigation in other areas may become apparent.

At the time the ORGDP program was started, the AEC's primary interest was in design and evaluation of plants for reprocessing high enrichment fuels. Therefore, the initial studies were made in problem areas concerned mainly with the hydrogen chloride-fluorination procedure for reprocessing zircaloy and aluminum alloy fuels. A small amount of experimental work was also done on the oxidatior fluorination method of processing graphite type fuels. With the change of emphasis to low enrichment power reactor fuel recovery, the ORGDP components program is now centered on the three-step hydrogen chloride decladding, uranium dioxide pellet oxidation, and fluorination method developed for zircaloy clad uranium dioxide fuels. As time permits, experimental studies related to the hydrogen fluoride-oxygen decladding procedure for stainless steel or zircaloy clad fuels are also being carried out.

Program results and status are summarized below.

MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES

Because of the unusual sequence of atmospheres in a single system, only scant corrosion data are available in the literature. For this reason, exposure tests are being made to determine which materials are suitable for the various volatility processes described earlier. To date, nickel-201 appears to be the only choice for a fluid-bed reactor in which fluorination is to be carried out at temperatures up to 550°C. Nickel-200 has good corrosion resistance, but the ASME pressure vessel code allows nickel only as the low carbon nickel-201 at the temperature level of the process. Both nickels appear satisfactory from a corrosion standpoint for alternating hydrogen chloride-fluorine atmospheres. Tests have not yet been made to simulate the conditions for the three-step hydrogen chloride plus oxygen-fluorine process for low enrichment zircaloy-clad fuels.

Duranickel, a nickel alloy containing a small amount of aluminum, is slightly less corrosion resistant to the hydrogen chloride-fluorine exposure than nickel-200 and nickel-201 but should be acceptable for flange material. Flanges should operate at a somewhat lower temperature than that required for the reaction vessel.

Corrosion rates of nickel-201, nickel-200, and Duranickel are also adequately low under the process conditions expected in the hydrogen fluoride-oxygen fluorination process.

Commercially available porous nickel filter material has good corrosion resistance in alternating hydrogen chloride-fluorine atmospheres. Monel filters are satisfactory for the hydrogen fluoride plus oxygen-fluorine system.

Corrosion resistance of all molybdenum and chromium containing alloys was relatively poor in both the hydrogen chloride-fluorine and the hydrogen fluoride plus oxygen-fluorine atmospheres.

PROCESS AND REACTOR STUDIES

The program in this area is related to the various chemical methods involved in converting reactor fuels to the desired volatile form. Since the chemistry of the various processes has in general been proved feasible by National Laboratory investigations, ORGDP work will be concerned mainly with establishing firm engineering information regarding reactor performance, configuration, and sizing. In the course of this work and during evaluation of system components, information on the flow sheet reactions will also be accumulated.

In conjunction with studies of filters for a high enrichment zirconium alloy element reprocessing system, tests were made which indicated that the small amount of oxygen contaminant in nitrogen or argon diluents will convert uranium metal to a finely divided oxide in the presence of hydrogen chloride and hydrogen. In other filter tests related to the hydrogen fluoride plus oxygen-fluorine process, a by-product of the filter investigation was a verification of the stainless steel oxidation results obtained at Argonne and Brookhaven National Laboratories.

To aid in the design of larger fluid-bed reactors for low enrichment fuels, fluidization of the various materials concerned is being observed in transparent columns. In one test, it was shown that complete separation of alumina and stainless steel oxidation residue by elutriation was not feasible. Removal of the coarse stainless steel oxidation products before fluorination would probably have made control of that step easier in addition to lowering fluorine costs and decreasing certain contaminants which form volatile fluorides, such as chromium and molybdenum.

Another study with a bed of simulated oxide pellets and alumina indicated that movement of the alumina diluent around most of the pellets was very poor. Channeling of a major portion of the gas through a small part of the bed was observed, thus indicating that heat transfer and gas contact problems may be serious in a large reactor during the pellet oxidation step. Although the total quantity of heat released by this reaction is relatively small (compared with the fluorination step), National Laboratory experience has shown that temperature excursions can still occur and that incomplete attrition of the pellets results.

A semiworks scale head-end fluid-bed reactor is being designed and will be constructed to study the decladding, fuel pellet oxidation, and fluorination operations. The unit will be 10 inches in diameter by 11 feet high with a 3-1/2-foot long, 5-inch diameter section at the bottom. The purpose of the reduced diameter of the lower portion of the bed is to provide a relatively high gas velocity through the settled bed of oxide fuel pellets, thus improving heat transfer and mobility of the alumina diluent. Tests will also be made without the 5-inch diameter section for purposes of comparison, and if indicated desirable, various gas

entrance configurations will be evaluated, as well as different bottom section designs. Outlet gas cooling and filtering will also be studied in this system. In addition to the semiworks fluid bed, an 8-inch diameter Plexiglas unit is being assembled to study gas entrance configurations and to observe fluidization characteristics with various types of fuel modules.

OUTLET GAS FILTER STUDIES

Studies are being made in a small fluid-bed loop to evaluate sintered metal filters for use in the fluid-bed reactor gas outlet. Both bench-scale corrosion tests and fluid-bed tests indicate that commercially available sintered nickel filter material will withstand cyclic exposure to hydrogen chloride and then to fluorine at the expected temperatures. Fabrication of a tube by rolling and welding appears to be a problem, however, as all welds have cracked after exposure. Preliminary tests on a molded (seamless) tube made by the Purolator Corporation are encouraging.

A test was also made which showed that sintered Monel filter tubes are suitable for the hydrogen fluoride plus oxygen-fluorine atmospheres required for stainless steel clad ceramic fuels.

PRODUCT PURIFICATION, SORPTION-DESORPTION SYSTEM

As contemplated, a portion of the fission product contamination will be removed from the uranium hexafluoride product by sorption on sodium fluoride heated to 400°C. Further purification is also possible by sorbing all the uranium hexafluoride on sodium fluoride held at 100°C. and allowing other impurities to pass through the bed. Studies are being made to determine the best type of sodium fluoride pellet to use for a batch sorber, to optimize both sorption and desorption conditions, and to evaluate traps designed for production use. At the present time, a temperature of 100 to 120°C. appears best for complete sorption of the uranium hexafluoride, while 400°C. is ample for desorption. All types of sodium fluoride pellets studied to date gradually break down into powder with repeated sorption-desorption cycles. Tests are also in progress to evaluate a production-scale pellet trap of annular design.

A fluid-bed system which appears capable of continuously sorbing large quantities of uranium hexafluoride has been developed for another project at the ORGDP. The uranium hexafluoride-containing gas is passed through a stirred fluid bed into which sodium fluoride powder is added continuously. Essentially complete stripping of the uranium hexafluoride is effected, and the powder overflow is transported to a ribbon flight screw where it is heated to recover the uranium hexafluoride. The regenerated sodium fluoride is then returned to the fluid bed to complete the cycle. The pilot-plant unit has been operated for a sufficient time to show that the process is workable; additional studies are required to determine capacity and optimum operating conditions.

CONNECTORS

Remotely operable connectors capable of maintaining gas-tight seals under process conditions will be required on major equipment items. Flange and gasket type seals utilizing double gaskets with a pressured buffer to monitor leakage are being considered for this use. Age hardened Duranickel appears to have adequate corrosion resistance and hardness for use as a flange with a nickel gasket. Preliminary temperature cycling tests in an inert atmosphere indicate that commercially available Marman Conoseal flanges made of this material are satisfactory for the alternating high and low temperature conditions. In view of the high cost of these units, however, studies are in progress to evaluate standard flat-faced flange designs.

COMPRESSORS

To reduce reactant usage in a reprocessing plant, gas recycle will probably be used in both the hydrochlorination and fluorination steps. The only commercially available compressor which will meet the process requirements is the diaphragm type unit. Such a machine, a Corblin compressor, has been purchased and is undergoing performance tests.

The diaphragm compressor has several undesirable features for use in a remote maintenance plant. These are (a) amplitudes of vibration are inherently high, making use of flexible connectors mandatory; (b) periodic replacement of diaphragms is necessary; and (c) flow rates are easily affected by malfunctioning of the check valves or by accumulations of small amounts of gas in the hydraulic fluids. In addition, flow rates are basically low, and relatively large and expensive units would be required.

A potentially better compressor from the standpoints of initial cost and maintenance is the peripheral type which is being studied at the ORGDP for other applications. Performance data have been obtained which demonstrate that a two-stage peripheral machine utilizing a 10-inch diameter impeller operating at 11,000 rpm. will meet the requirements for hydrogen chloride and fluorine recycle systems. In addition to the impellers, the compressor will include a shaft seal and an externally mounted bearing system and driving motor. Tests indicate that a low clearance bushing seal and grease packed high precision angular contact bearings should give satisfactory performance. A prototype unit is presently under construction and will be evaluated under process conditions.

REACTOR FABRICATION PROCEDURES - WELDING STUDIES

A procedure has been developed for making welds of nickel-201 rod which will meet the conditions specified in pressure vessel codes.

DISCUSSION

ENGINEERING STUDIES

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Studies of the economic technical feasibilities of various processes for recovery of fissile material from irradiated nuclear reactor fuels are being performed to provide guidance for the associated development programs. These studies are aimed at arriving at conceptual plant designs with estimates of cost and evaluations of potential scale-up problems.

Coupled with this effort is a systems analysis program designed to summarize the large number of process alternatives and problems and to indicate work areas which should be emphasized in the integrated overall program.

Engineering studies for power reactor fuels and high uranium enrichment materials are described briefly in this report. Included also are more detailed calculations relating to specific problems, such as alumina bed usage economics, bed temperature rises due to radioactively generated heat, and criticality considerations for high uranium enrichment fuels.

Historically, the ORGDP development programs began with evaluation of processes for the high enrichment fuels. This followed logically from the National Laboratory volatility programs which had been largely aimed at the spent high enrichment fuels because of their relatively early availability for processing. It is not surprising, however, that the volatility technology, engineering, and experimental results for high enrichment fuels are, to a substantial degree, useful in the low enrichment power reactor fuel program.

HIGH ENRICHMENT FUELS

Engineering studies have been performed for the aluminum-uranium, zirconium-uranium, and graphite matrix high enrichment fuels. Processing of these materials using the fluid-bed reactor systems bears many similarities to work for low enrichment fuels. The major difference is, of course, the necessity for recovering plutonium from the low enrichment fuels. Technology, however, for low enrichment fuels processing has been relatively incomplete because much remains to be learned about plutonium hexafluoride handling and conversion to solid product.

Initial engineering analyses were carried out on the technology and economics of high enrichment fuel processing because of the advanced

"state-of-the-art". The analyses were used primarily for program planning purposes. The general conclusions were that volatility processes were at least competitive with aqueous routes and that the fluid-bed volatility approach coupled a high probability of ultimate success with more versatility than is available with the major competitor, molten salt processing. Additionally, fluid-bed systems were recognized to be more adaptable than the molten salt sequence to low enrichment fuel treatment for plutonium recovery.

Following these initial analyses, a more comprehensive study was undertaken covering highly enriched aluminum, zirconium, and graphite base fuels and using the latest estimations of generation rate. This study is now in progress, and a few details relating to the processing schemes and time cycles follow.

The processes for both the aluminum and zircaloy fuels involve hydrochlorination to remove the aluminum or zirconium and tin as volatile chlorides. The hydrochlorination off-gas is fed to a fluid-bed pyrohydrolyzer for conversion of the clad compound to solid oxide in oxychloride form. The uranium remains behind as a nonvolatile chloride and may be fluorinated immediately or after treatment of the bed with hydrogen fluoride to replace the chloride with fluoride. This latter step is included to prevent generation of chlorine trifluoride or chlorine which could lead to problems in the off-gas caustic scrub system. Both single-vessel and multiple-vessel reactor lines are being considered.

Some fission products, notably zirconium, ruthenium, niobium, iodine, and the noble gases, are expected to be wholly or partly volatilized in the hydrochlorination. The zirconium, ruthenium, and niobium are expected to be retained in the pyrohydrolysis reactor bed, while the noble gases will pass through to the vent. Iodine may tend to accumulate in the hydrogen chloride recycle system until blown down to the neutralization system.

Technetium, ruthenium, molybdenum, and tellurium, as well as plutonium and neptunium, are the primary contaminants expected to be found in the reactor off-gases during fluorination. A combination of sodium fluoride and magnesium fluoride sorption is expected to be effective in removing these elements excepting tellurium. Although tellurium is expected to be partially removed by caustic scrubbing and exposure to hot nickel or carbon, it may pose a vent problem.

In the single-vessel process, hydrochlorination, hydrofluorination, and fluorination steps are all carried out in the same fluid bed. The multiple vessel line originally considered had three separate units, one for each chemical step; however, it is now felt that equipment use scheduling will permit both hydrofluorination and fluorination to be carried out in the same vessel.

Table I compares time schedules for the two schemes. In each case, three charges of elements are hydrochlorinated before hydrofluorinating for chloride removal in the single-vessel case or transfer to the hydrofluorinator-fluorinator in the multiple-vessel case.

TABLE I

CYCLE TIMES FOR ZIRCONIUM AND ALUMINUM FUELS

Operation	Reactor Time Required, hours	
	Single-Vessel System	Multiple-Vessel System
Transfer Aluminum Oxide In, Charge Fuel, Adjust Temperature	2	2
Hydrochlorinate	12	12
Purge, Charge Fuel, Adjust Temperature	2	2
Hydrochlorinate	12	12
Purge, Charge Fuel, Adjust Temperature	2	2
Hydrochlorinate	15*	15*
Purge, Adjust Temperature, or Transfer Bed Material Out	1	2
Total Hydrochlorination Time	46	47
Transfer Bed Material In, Adjust Temperature	0	1
Hydrofluorinate	3	3
Purge, Adjust Temperature	1	1
Fluroinate	4	4
Purge, Sample, and Analyze†	0	3
Purge, Transfer Bed Material Out	1	1
Total Hydrofluorination and Fluorination Time	9	13
Cycle Controlling Time	55	47

* A 3-hour tailoff period is included in the final hydrochlorination time to assure complete reaction of the thicker sections of the fuel modules.

† The bed material from the single vessel system is transferred to a surge hopper for sampling and analysis; the bed material from the multiple vessel process is sampled in the fluorinator and is held there until sample results are obtained.

The overall cycle time for the single-vessel option is 55 hours. This allows processing of aluminum fuels in a single line at the rate of 5.13 kg. of uranium per day. With an assumed load of 1,000 kg. of uranium per year from this source, about 195 on-stream days per year are thus required. Assuming only 260 on-stream days are available per year to allow for downtime for maintenance, inventory, and campaign accountability purposes, 65 on-stream days per year are left for the zirconium-base fuels. This appears sufficient, so a single line is used to handle both loads.

The overall cycle time for the hydrochlorinator in the two-vessel plant is only 47 hours. The hydrofluorinator-fluorinator reactor processing time is only 13 hours per overall cycle; thus, the hydrochlorinator scheduling is controlling. Using the same size reactor for the hydrochlorination step as in the single-vessel plant, the processing rate is 6.01 kg. of uranium-235 per day for the aluminum fuels. This would apparently allow processing of about 17% more fuel in the two-vessel plant, thus making a nominal decrease in reactor size possible.

In the event that processing loads are increased, another possibility for the two-vessel flow sheet calls for one hydrofluorinator-fluorinator servicing two or more hydrochlorinators; however, this arrangement might be undesirable from the standpoints of accountability and criticality control. Perhaps the biggest advantage of the two-vessel system would be to remove some of the restrictions on the material of construction. For example, Inconel can be considered for use in both the reactor and porous metal filter systems for hydrochlorination if not subsequently exposed to fluorine. Sintered Inconel filter tubes have been used at ANL in some of the hydrolyzer work. The corrosion performance of both porous and structural nickels may be improved if exposed only to hydrogen fluoride containing a small amount of hydrogen chloride and to fluorine. Monel may even be satisfactory for this last combination.

The graphite fuel reprocessing is best done in a separate line. The fuel may be broken into chunks and fed semicontinuously to a relatively small oxidizer fluid bed; i.e., perhaps 10 inches in diameter. Combustion proceeds readily at 700°C., and little unconsumed graphite, other than newly fed chunks, is present. When enough uranium has accumulated in the alumina diluent, the bed is transferred to a fluorination fluid bed. Most of the uranium comes off readily in fluorination; however, there is a decreasing rate at the end so that several hours are required for the removal of the last few percent.

The present concept of a multipurpose volatility plant thus includes one reactor line for processing zircaloy and aluminum alloy fuels and a second reactor line for handling the graphite-base material. Each line would have its own specific auxiliaries, such as the pyrohydrolysis reactor and hydrogen chloride recycle for the zircaloy and aluminum alloy fuels and combustion off-gas system for the graphite-base materials. Since the lines would be expected to be operated at the same time during a substantial portion of the year, each would have its own cold trap system.

Process flow sheets and conceptual equipment designs and layouts have been essentially completed. Estimates of cost and preparation of the report are in progress.

LOW ENRICHMENT POWER REACTOR FUELS

The present volatility program emphasis is on developing processes for recovery of uranium and plutonium by volatilization as the corresponding hexafluorides from low enrichment zircaloy and stainless steel-clad uranium dioxide power reactor fuels. Consistent with this goal, the major part of the engineering study effort is now being directed toward processes for the low enrichment fuels. Since it appears that the zircaloy-clad fuels may predominate in the future, the initial study is aimed at these materials. Before describing a tentative view of the conceptual plant system, a brief look at process alternatives is warranted. Figures 1 and 2 show the major potential flow sheet routes in simplified schematic fashion, omitting decisions which may be settled on an essentially economic basis; e.g., recycle requirements for gases and bed solids, process equipment necessities such as filters and heat exchangers, number of reactors in a processing line, and order of purification and recovery steps. The heavy connecting line shows the path of the present reference flow sheet for the zircaloy-clad uranium dioxide fuels.

Zircaloy-Clad Fuel Process

In the present reference flow sheet for zircaloy-clad fuels, figure 3, the initial processing step after mechanical removal of end hardware is hydrochlorination at 400°C. with the fuel element(s) immersed in a fluidized bed of inert powder; i.e., alumina. This treatment volatilizes zirconium as the tetrachloride and tin as the bichloride. Reaction with the uranium dioxide is expected to be minimal. The decladding off-gas is conducted to a second fluid-bed reactor where the volatile cladding compounds are reacted with water vapor at about 350°C. to convert them to solids for ease in storage. Except for the noble gases and iodine, radioactive substances vaporized by the hydrochlorination would be expected to be fixed on the pyrohydrolysis bed material, thus leaving a relatively clean hydrogen chloride-containing effluent stream. Since the hydrogen chloride is not expected to attack the uranium dioxide to a significant degree, most of the fission product activity is not expected to be reacted. That remaining after fluorination could be volatilized in the subsequent hydrochlorination in the likely event that the bed material is reused. The hydrogen chloride consumed in the head-end fluid bed is reconstituted in the hydrolysis process and, along with the excess hydrogen chloride, may be recycled back to the head-end fluid bed.

After conclusion of the declad step, the uranium dioxide solids will be in an essentially static bed at the bottom of the reactor due to their high density and relatively large size. A diluent oxygen stream is used to convert the uranium dioxide to fine urano-uranic oxide powder which will fluidize along with the diluent. The pellet breakup will also allow conversion of the plutonium and fission products to fine powders. Fluorine is used to react with these materials to produce the uranium hexafluoride

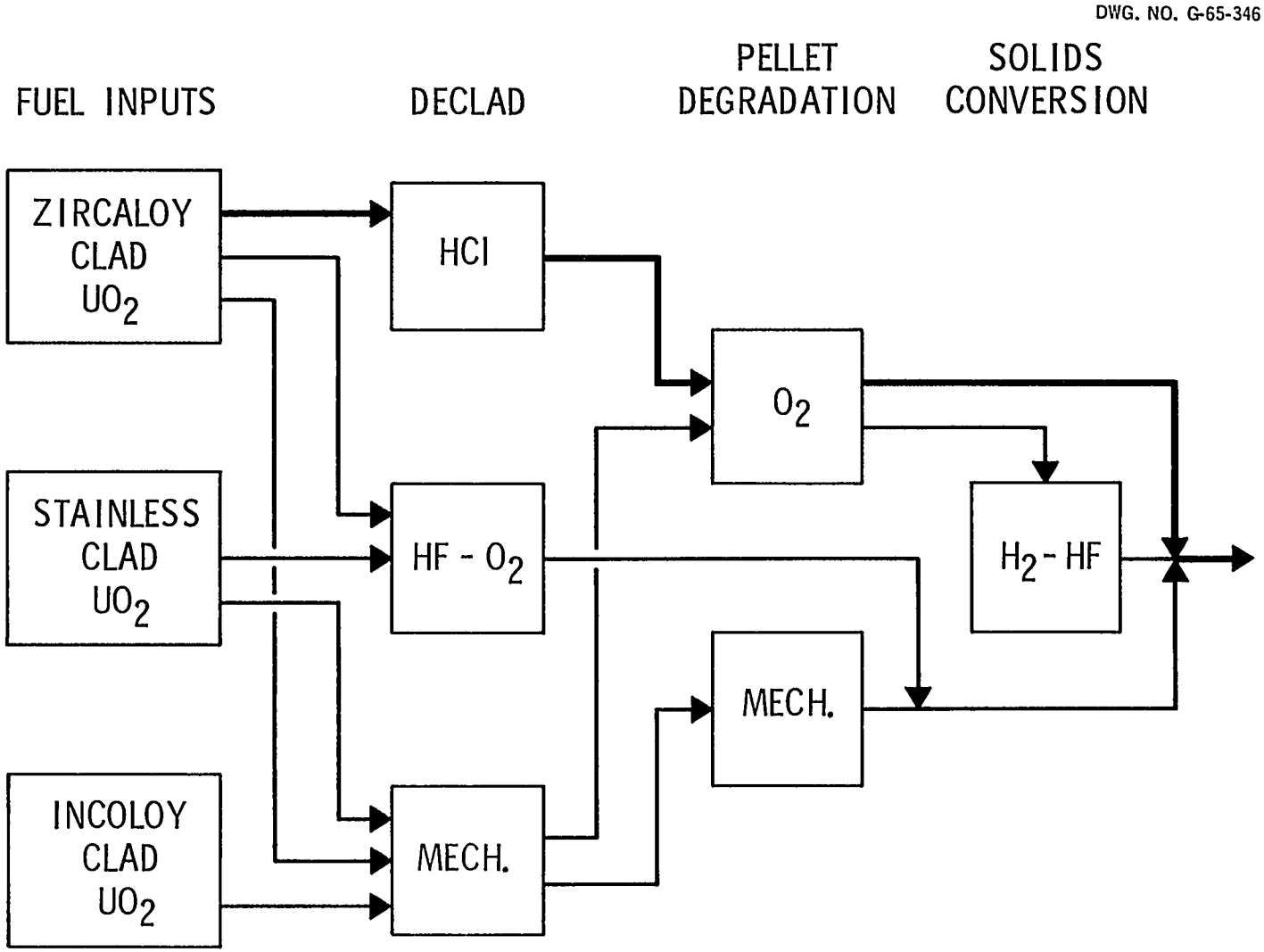

Figure 1
DECLADDING AND CHEMICAL PRETREATMENT

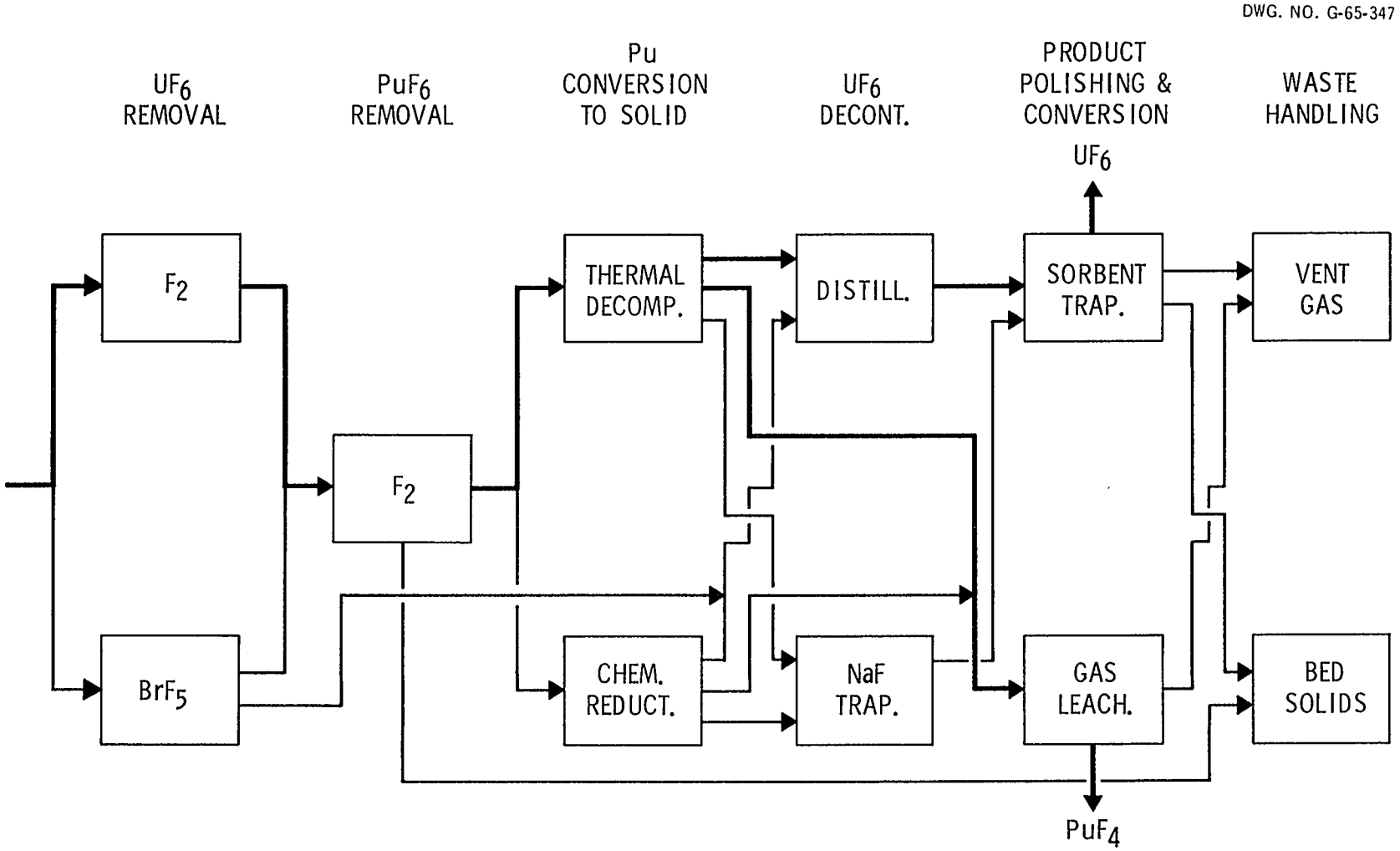

Figure 2

FLUORINATION AND PRODUCT RECOVERY

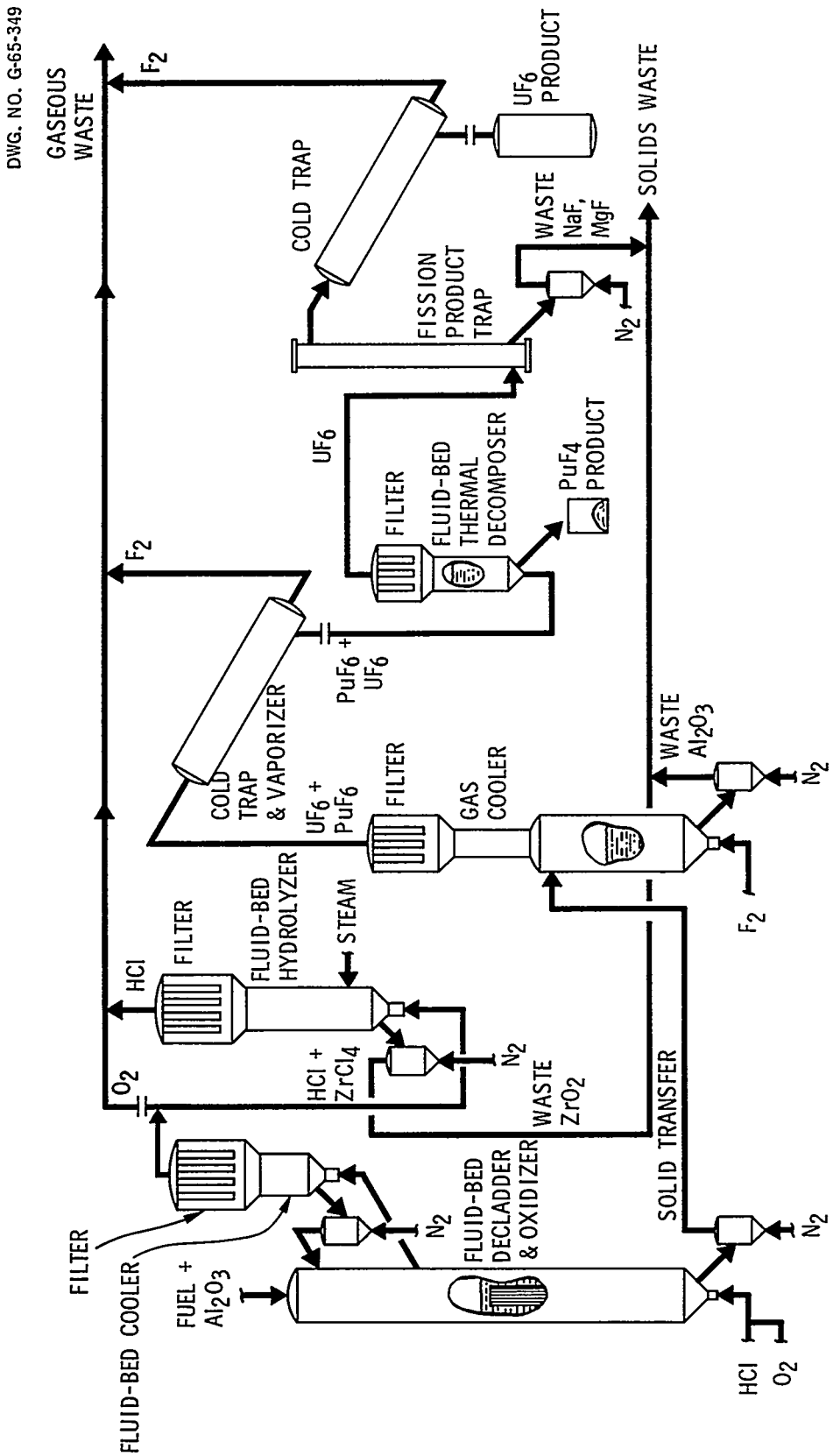

Figure 3
POWER REACTOR FUEL REPROCESSING PLANT

and plutonium hexafluoride. The fluorination reaction is initially conducted at 400°C. to remove most of the uranium along with a relatively small proportion of the plutonium. The temperature is then increased to 500 to 550°C., and the remainder of the plutonium is volatilized.

As subsequently discussed in more detail, it is presently planned to use a two-diameter fluid bed such that high gas velocities can be utilized in the lower smaller diameter in which the pellets will fall after decladding. This high velocity should result in improved powder carryout and heat transfer in this zone, while at the same time, the velocity will be less in the upper bed section with the larger diameter so that excessive elutriation does not occur.

The product gas stream is passed through a cold-trapping system for removal of plutonium hexafluoride and uranium hexafluoride. The plutonium hexafluoride-uranium hexafluoride mixture, along with fission product fluorides also removed at this point, is fed to a thermal decomposer in which plutonium tetrafluoride solid product is deposited. The uranium hexafluoride is then distilled, and the product fraction is passed through sorbent traps for final cleanup. The fission product streams from the distillation may be packaged for storage by chemisorption on a suitable solid or by other suitable means.

Some basic information remains to be developed with regard to this flow sequence. The uranium processing aspect seems to be demonstrated from a technical standpoint, although additional information is needed for proper scale-up. The ANL work to date has also given a degree of confidence that the plutonium can indeed be volatilized and transferred. Additional effort will be required to show that actual fuel materials can be so treated and to provide better operational parameters. Further, studies of distillation of plutonium hexafluoride-bearing material and of thermal decomposition for plutonium tetrafluoride production necessary to provide design data are incomplete. Fission product chemistry investigations on a process scale with irradiated fuel water are required to validate predictions as to which will be volatilized in each step and where these will come out in the process.

Stainless Steel-Clad Fuel Process

The present preferred process for stainless steel-clad uranium dioxide fuels utilizes a hydrogen fluoride-oxygen gas at 600°C. to spall off the cladding and rusty fragments. The uranium dioxide pellets are concurrently broken up by oxidation into fine powder and are then converted to uranyl fluoride and uranium tetrafluoride. The maximum reaction rate appears to occur when a 40% hydrogen fluoride concentration is employed; however, plant operation may require use of lower or higher concentration for reaction and heat release control. The clad is not volatilized except for a portion of the chromium converted to fluoride. A large part of the clad residue is relatively coarse, even containing slivers as long as 1/2 inch or so. The degree of conversion of the clad and the uranium to oxyfluorides and fluorides depends on the length of exposure to hydrogen fluoride. The fluorination step proceeds readily enough,

except that some difficulty may be encountered in control of reaction heat removal in the zone in which the coarse material accumulates. Use of the two-diameter fluid bed and careful control of the fluorine concentration in the early stages of the reaction should minimize operating difficulties. Fluorination breaks up the coarse clad material to a fine powder so that bed transfer should not be impeded.

The uranium and plutonium recovery and purification aspects of stainless steel-clad fuel reprocessing would be about as stated for the zircaloy materials.

Interhalogen Flow Sheet

Flow sheets employing bromine pentafluoride for removal of the uranium, as indicated by figure 4, are now being evaluated. The thermodynamics indicate that plutonium cannot be volatilized in significant amounts by reaction with bromine pentafluoride, while uranium can be essentially completely removed*. Plutonium would be volatilized by reaction with elemental fluorine in the subsequent step. Thus, a clean separation of uranium and plutonium in the fluid-bed fluorinator should be possible, and simplifications in the product handling system could be achievable as compared to that for the reference flow sheet which uses fluorine only. Additionally, the rate of fluorination of uranium salts with bromine pentafluoride is apparently faster than with fluorine, and the heat release is also lower. This last feature of use of bromine pentafluoride may not be exploitable in two-zone oxidation-fluorination, since the oxidation step may well be controlling. Against these advantages must be weighed the complications involved in having (a) an off-gas stream containing bromine pentafluoride, bromine trifluoride, and uranium hexafluoride; (b) a reaction system for conversion of bromine trifluoride to bromine pentafluoride; and (c) a sorption or distillation separation system for purifying the uranium hexafluoride from bromine compounds.

The use of bromine fluorides for nuclear fuel reprocessing had been studied previously but mainly for metallic uranium or alloy type fuels. From these efforts, data are available for many of the component properties†, table II.

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* Experimental studies are in progress at Argonne National Laboratory to verify this conclusion and provide kinetic data.

† Stoller, S. M., and Richards, B. B., editors, Reactor Handbook, Volume II, Fuel Reprocessing, Interscience Publishers, Inc., New York (1961).

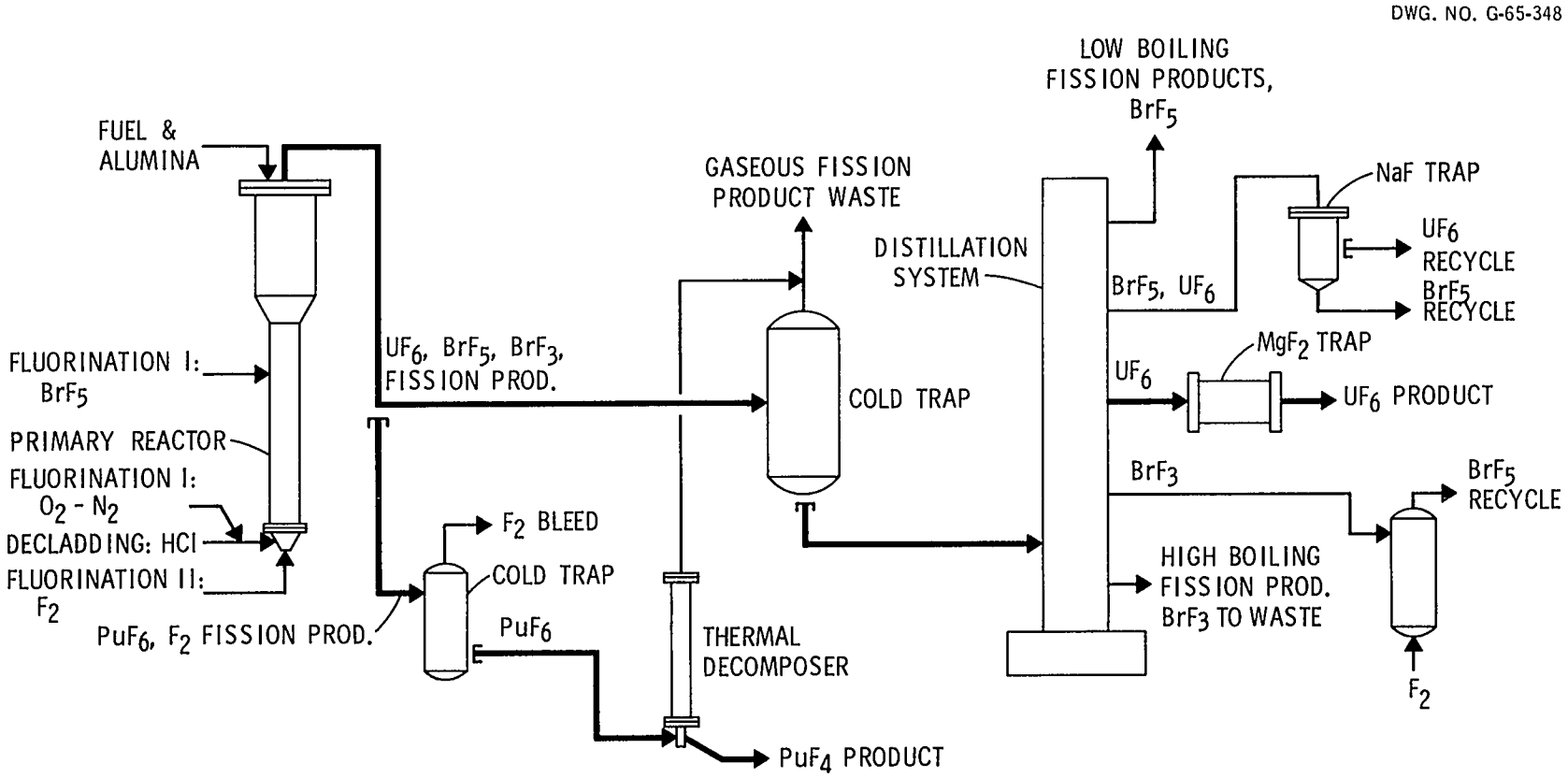

Figure 4

INTERHALOGEN REFERENCE FLOW SHEET

TABLE II

PHYSICAL PROPERTIES OF
BROMINE PENTAFLUORIDE, BROMINE TRIFLUORIDE, AND URANIUM HEXAFLUORIDE

Property	Uranium Hexafluoride	Bromine Pentafluoride	Bromine Trifluoride
Molecular Weight	352	174.92	136.92
Melting Point, °C.	64.02	-60.5	8.77
Normal Boiling Point, °C.	56.54*	41.3	125.75
Triple Point Pressure, mm. Hg	1137	1.7	2.4
Critical Constant (estimated)			
Temperature, °C.	230	213	340
Pressure, atmospheres	45.5	47	70
Heat of Fusion, kcal./mole	4.588	1.74	2.875
Heat of Vaporization, kcal./mole	6.82	6.88	10.235
Density, g./cc.			
Solid	5.06(25°C.)	3.09(-61°C.)	3.23(8.8°C.)
Liquid	3.67(64°C.)	2.4604(25°C.)	2.803(25°C.)
Solubility of Uranium Hexafluoride in Bromine Pentafluoride at -40°C., g.UF_6/g.BrF_5	0.163	-	-
Vapor Pressure of Pure Component at -40°C., mm. Hg†	0.3	8.5	0.05

* Uranium hexafluoride sublimes at normal atmospheric pressures.

† This should be about the same as partial pressure of solute above a saturated solution at this temperature.

Liquid-solid phase diagram information is available for the binary systems uranium hexafluoride-bromine pentafluoride and uranium hexafluoride-bromine trifluoride. Liquid-vapor equilibrium diagrams are available for the binary systems but not for low total pressures. Ternary phase equilibrium data have not been found in the literature. Based on the available data, the following comments can be made:

1. Cocurrent condensation of a liquid mixture of bromine pentafluoride, bromine trifluoride, and uranium hexafluoride with high recovery

from a dilute gas stream requires that the bromine pentafluoride be in high concentration in the mix. For a reactor off-gas containing 3% uranium hexafluoride, 10% bromine trifluoride, and 3% bromine pentafluoride, precipitation of uranium hexafluoride and bromine trifluoride would probably occur at temperatures not much below the uranium hexafluoride triple point; however, a mixture containing 90 mole percent bromine pentafluoride, 5 mole percent bromine trifluoride, and 5 mole percent uranium hexafluoride is expected to be a liquid at minus 30°C., at which temperature, the total vapor pressure of the solution would be about 10 mm. Hg, and the uranium hexafluoride partial pressure would be about 1 mm. Hg. The freezing point of a liquid containing 95% bromine pentafluoride and 5% uranium hexafluoride would, however, be about minus 53°C., at which point, the uranium hexafluoride vapor pressure would be about 0.05 mm. Hg.

2. Continuous distillation of a bromine pentafluoride, bromine trifluoride, and uranium hexafluoride mix to produce purified uranium hexafluoride with high recovery would appear to require two columns, since the uranium hexafluoride is intermediate in volatility.

3. Obtaining a purified uranium hexafluoride product from the bromine pentafluoride-uranium hexafluoride mix may be relatively simple, since the relative volatility of bromine pentafluoride to uranium hexafluoride at the low bromine pentafluoride end exceeds two. Purifying the bromine pentafluoride from uranium hexafluoride by distillation will be more difficult but probably less important, since some recycle of uranium hexafluoride in this stream may be tolerated. British reports of an azeotrope at a significant uranium hexafluoride concentration are discounted by Argonne National Laboratory work*.

4. Stripping of the lower boiling bromine trifluoride from uranium hexafluoride to achieve concentrations of 1 ppm. bromine† may require a considerable number of transfer units in a continuous distillation unit. Further data as to the activity coefficient of bromine trifluoride at the low bromine trifluoride concentration end may be needed.

5. Kinetics of conversion of bromine trifluoride to bromine pentafluoride by reaction in a gaseous state with fluorine are such that moderately high conversion efficiencies, i.e., 95 plus percent, may be obtained even from fairly dilute streams. Ultrahigh conversions, i.e., so that less than 1 ppm. bromine as bromine trifluoride (uranium basis) remains, may require a fairly large reactor or may even be prevented by equilibrium considerations. It appears that the best solution of the distillation problem would be to eliminate bromine

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* Ellis, J. F., Johnson, K. D. B., J. Inorg. Nucl. Chem., 6, 194 (1958).

† This is the present specification limit for return of uranium hexafluoride to the AEC. Recycle directly to fuel fabrication operations might allow a considerably higher specification limit and considerably ease the separation problem.

trifluoride from the system by prior reaction possibly helped along by injection of some fluorine into the still reboiler to ensure reaction completion.

The selection of a process flow sheet depends not only on feasibility but also on economics. Accordingly, several flow sheet arrangements which are all thought to be technically feasible have been prepared for preliminary evaluation.

These flow sheets all presume hydrogen chloride decladding for removal of the zircaloy clad and then two-zone oxidation-fluorination, using bromine pentafluoride, for volatilization of the uranium. Plutonium would then be recovered by fluorination with elemental fluorine. The differences among the arrangements lie in the off-gas handling portion of the two-zone oxidation-fluorination step. The oxidation-fluorination operation in the main reactor would be essentially the same as before except that bromine pentafluoride would be used, and thus no plutonium would be volatilized. The off-gas will be mostly oxygen and nitrogen with, on the average, about 3 mole percent uranium hexafluoride, 3 mole percent bromine pentafluoride, and 10 mole percent bromine trifluoride.

The variations are related to the location of the step for fluorination of bromine trifluoride to bromine pentafluoride in the process scheme, i.e., before and after separation of the condensables from the head-end fluid-bed reactor off-gas, and to the selection of the major uranium hexafluoride purification process; i.e., sorption or distillation. An additional variant can be introduced depending on whether a flash cooler-condenser requiring substantial amounts of bromine pentafluoride liquid recycle is employed to remove condensables from the gas stream at such high relative bromine pentafluoride concentrations that uranium hexafluoride and bromine trifluoride are dissolved. In some flow sheets, particularly if distillation is the purification method, this strategem would probably reduce the size of the necessary cold-trapping systems.

Work is in progress to complete the conceptual sizing of the equipment required for each of these flow sheets. Comparison of the equipment requirements will hopefully lead to elimination of some of the alternatives so that more detailed comparisons can be made, including the reference flow sheet using fluorine alone in this group.

Head-End Fluid-Bed Reactor

The fluid-bed halogenator is probably the key unit in the volatility process for power reactor fuels. It must serve satisfactorily in processing highly radioactive material through rigorous chemical treatment under conditions that are far from those usually considered ideal for fluidization. These conditions include the heterogeneous situation during decladding when the fuel bundle is immersed in the fluidized bed of alumina. Furthermore, for the zircaloy fuels, the oxidation of uranium dioxide takes place in a packed bed of fuel pellet fragments with the alumina grain fluidized in the interstices.

In the first case noted above, the main question appears to be how freely the fluidized alumina bed and the gas move through the tube bundle. This circulation is necessary for both heat removal and reaction reasons. Test work to date has been limited and on a relatively small scale; i.e., nine tubes*. In the zircaloy-clad class, a single Dresden-type module has 36 tubes, and proposals are being made for still larger modules. Oyster Creek is scheduled to have 64 tubes per module. Stainless clad fuels have as many as 169 tubes per module. A production reprocessing batch charge for the zircaloy-clad fuels as presently contemplated would be on the order of 150 tubes. With nine tubes, the center tube has only one tube between it and the free bed. Thus, the dynamic and reaction situation of interior tubes located many rows from the free bed has probably not been achieved. The pellet oxidation studies have been mainly on a 3-inch diameter bed with some work on a 6-inch diameter unit.

As discussed in the component section that follows, a semiworks reactor intermediate in scale between the plant unit and the present test units has been proposed.

A two-diameter reactor is contemplated so that high gas velocities may be attained in the pellet oxidation zone while having a normal velocity in the upper portion of the bed. For example, the present conceptual plant reactor is 24 inches in diameter in the upper part of the bed which gives room for charging fuel elements side by side to a total of 500 to 1000 kg. of uranium and allows operation with an outlet gas velocity less than 1 ft./sec. for the flow sheet gas quantities. At the same time, the lower portion of the reactor is only 1 foot in diameter which, after giving effect to pressure drop, still permits operation at 1.5 to 2.0 ft./sec. gas velocity to aid in fines carryout from this zone. The smaller diameter also allows for a greater wall-area-to-bed-volume ratio for heat transfer.

Disadvantages of the two-zone approach that will have to be considered in the final optimization analyses are (a) an adverse effect from the greater overall reactor height on equipment and building expense, (b) the higher gas pressure drop that would be incurred, (c) possible compaction of the pellets at the bottom of the deep pellet bed, and (d) prevention of fines transfer from the deeper pellet bed to the upper fluid-bed zone by an impingement filtration action.

With regard to mechanical details, it appears that nickel is the leading and virtually only candidate material of construction on a corrosion resistance basis for a vessel in which hydrochlorination, oxidation, and fluorination are performed; i.e., where the single-vessel approach is used for the reactions in the fluid bed. If fluorination were carried out in a separate vessel, Inconel could probably be employed for the hydrochlorination and oxidation phases. The fluorinator would be a

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* ANL experiments on a 25-tube bundle were scheduled as this report was in preparation.

second fluid bed, and the process would be called a two-vessel process. Either Inconel or nickel should have moderately good resistance to the hydrogen fluoride-oxygen gas mixture used for decladding stainless steel-clad fuels.

For the single-vessel process, the present specification concept is that low carbon nickel will be used for surfaces in contact with the process. Welding will be performed using low carbon nickel rod and a modified Heli-arc process. Except if needed for corrosion resistance, stress relief may not be required, particularly since the operating temperature will be near that used for stress relief. Inspection of welds will include dye penetrant and full X-ray. Pressure and leak testing will be required. The vessel design will be subjected to stress analyses per section III of the ASME code; however, stress values from section VIII will be employed.

Radioactive Heat Generation

Radioactive heat generation poses a problem in (a) fuel charging machinery, (b) the fluid bed in removal of heat from newly charged elements should fluidization cease in this area, and (c) the contaminated bed solids should fluidization fail for the whole bed.

Results of calculations covering the centerline temperature rise rate for the settled alumina bed are given in table III. The 9-watt per liter case is valid for 1 to 2 bed cycles with fuel which has been cooled 130 to 165 days after irradiation to 10,000 to 25,000 Mw.-day/metric ton of uranium. With the present shipping regulations, this much cooling time would probably be required for safety and economy. The 90-watt per liter case was chosen to represent five bed recycles for processing the 30-day cooled fuel. Since the bed material conductivity is not known, values of 0.25, 0.5, and 1.0 pcu./hr.-ft.-°C. were used in the calculations.

TABLE III

TEMPERATURE RISE IN A 20-INCH DIAMETER
SETTLED BED WITH VOLUME HEAT GENERATION

Time, hr.	ΔT, °C.					
	Q = 9			Q = 90		
	k = 0.25	k = 0.50	k = 1.0	k = 0.25	k = 0.50	k = 1.0
1	13.9	13.9	13.9	139	139	139
2	27.8	27.8	27.5	278	278	275
4	55.0	55.0	48.6	550	550	486
8	113.9	97.2	70.5	1,139	972	705
16	194.4	141.6	80.5	1,944	1,416	805
Steady State	335.6	167.8	83.4	3,356	1,678	834

Notes: ΔT = Centerline Temperature Rise, °C.
k = Thermal Conductivity of Bed, pcu./hr.-ft.-°C.
Q = Heat Generation in Bed, w./l.
Specific heat used was 0.26 pcu./lb.-°C.
Density used was 135 lb./cf.

For the first 4 hours, the centerline temperature rise is about that which could be calculated for adiabatic conditions. Accordingly, for this period of time for the centerline temperatures, the actual value of the thermal conductivity is not important so long as it is less than 1.0 pcu./hr.-ft.-°C., and it does not matter if the wall temperature is held constant; i.e., whether heat is removed at the wall or not. While it is not feasible to put an upper limit on allowable alumina temperature now because the effect of solids residues (both radioactive and nonradioactive) on the caking tendency has not been established, it is reasonable that a temperature of perhaps 700°C. would be limiting. If the charging commences with the bed initially at 400°C., the numbers in table III indicate that the bed may be settled for 2 hours before centerline temperatures get too high, even with the higher power level alumina. It is also apparent that difficulties with sintering and even alumina melting could occur under extreme circumstances with the lowest value assumed for thermal conductivity of the bed. Calculations were also made to determine the temperature rise rate for a module immersed in a settled bed. A machine program was written to compute rod temperatures for a fuel element having an even, square array with the element being immersed in a bed of greater diameter than the diagonal of the array.

Calculations were made for a pseudo-Westinghouse module, 14 × 14 rods in dimension. The module was considered to be immersed in a bed 16 inches in diameter; i.e., about 6 inches longer than the diagonal of the cluster. The bed was assumed to be initially at a uniform temperature of 350°C. and to be cooled through the wall by a heat transfer media at a tempera-

ture of 100°C. with a heat transfer coefficient of 10 pcu./hr.-sq.ft.-°C. The bed conductivity was taken at 0.25 pcu./hr.-ft.-°C., and the density and specific heat again approximated those for alumina. Although the chosen model does not precisely duplicate the contemplated reactor sizing, i.e., a bed of about 2 feet in diameter containing two 173-rod clusters side by side, it is thought to be sufficiently close to provide usable information. The calculation results are given in table IV. The two cases simulate the 130- to 165-day cooled material in a bed recycled about two times and the 30-day cooled element in a bed recycled five times. Significantly, for both cases for the innermost rod, the temperature rise is essentially adiabatic for at least 6 hours. The adiabatic temperature rises per hour are about 78 and 228°C. for case I and case II, respectively.

One conclusion from the calculations is that the temperature rise rates are large enough to impose significant problems, particularly with the shorter cooled, higher burnup material. Certainly the melting point of stainless steel, i.e., about 1400°C., would be a circumstance resulting in unusual operating difficulty, and the sintering of bed material, perhaps 700°C. or slightly higher, might be used as the restriction for more usual operating difficulty situations. A second conclusion is that calculation of adiabatic temperature rise rates is probably adequate for consideration of the problem; thus, much use of the machine program is not required. A few additional situations may be explored to determine the effect of use of a higher bed material conductivity, probably k = 1 pcu./hr.-ft.-°C, of smaller bed diameter, and of smaller modules. A memorandum has been prepared to cover in detail the radioactive heat generation calculations made to date.

Alumina Diluent and Bed Storage Costs for Power Reactor Fuel Processing

Calculations relating to the economics of bed recycling, including alumina cost, fuel cooling time before reprocessing, and waste storage investment using bin storage costs developed at the ICPP*, have been made. Some of the results are presented in table V. The 0.4 kg. alumina per kg. of uranium usage rate corresponds to about six bed recycles or, equivalently, a 16% drawoff after each cycle. The results in general indicate that, as might be expected, reduction of alumina usage is desirable from an economic standpoint. They also show that storage capital costs are of the same order of magnitude as the value of plutonium losses of 1%, which is the presently envisioned process loss limit. For example, for a fuel containing 10 kg. of plutonium per MTU, a high value for slightly enriched uranium fuels, a loss of 1% amounts to 100 grams per MTU, or about $1,000 per MTU. Thus, the incentive for increasing alumina utilization may lie as much in reduction in waste storage costs as in further increases in plutonium recovery efficiency.

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* Stevens, J. I., An Economic Evaluation of Ultimate Disposal of Liquid Radioactive Wastes by the Fluidized Bed Calcination Process, Phillips Petroleum Company, October 30, 1962 (IDO-14595).

TABLE IV

ELEMENT TEMPERATURE TRANSIENTS IN SETTLED BED
FOR 14 x 14 PSEUDO-WESTINGHOUSE MODULE
IN 16-INCH DIAMETER BED*

Time, hr.	ΔT, °C.			
	Case I†		Case II‡	
	Innermost Rod	Outermost Rod	Innermost Rod	Outermost Rod
0	0	0	-	0
0.5	40	36	115	109
1.0	80	67	230	211
2.0	160	117	460	401
3.0	240	161	690	577
4.0	320	202	920	745
6.0	479	284	1,380	1,062
8.0	638	366	-	-
11.5	911	507	-	-

* Rod diameter is 0.340 inch, and the rods are in a square pitch array with a center-to-center diatance of 0.452 inch. The actual element contains 173 rods with the same center-to-center spacing and rod diameter but with two offset rows accounting for the deviation from a 13 x 13 array. The boundary condition employs a wall heat transfer coefficient of 10 pcu./hr.-sq.ft.-°C. to a cooling media with a temperature of 100°C. The starting condition is a uniform bed temperature of 350°C. The cooling was sufficient to reduce the wall temperature below 350°C. in each case. The bed material is assumed to have a density of 135 pounds per cubic foot, a specific heat of 0.25 pcu./lb.-°C., and a thermal conductivity of 0.25 pcu./hr.-ft.-°C.

† Heat generation in rods is equivalent to 1 kw. per 100 kg. of uranium; heat generation in bed solids, 9 watts per liter. This may be considered to be the case for about two bed recycles for processing 130- to 165-day cooled material.

‡ Heat generation in rods is equivalent to 2.81 kw. per 100 kg. of uranium. Heat generation in bed solids is 90 watts per liter. This may be considered to be the case for perhaps five bed recycles for processing 30-day cooled material.

TABLE V

ALUMINA USAGE ECONOMICS

Cooling Time, days	Heat Release*, Btu./hr.-MTU	Al_2O_3 Requirements, kg./kg. U	Storage Volume, cu.ft./MTU†	Storage Cost‡, $/MTU	Al_2O_3 Cost§, $/MTU	Total, $/MTU
30	87,000	0.4	8.5	1,037	160	1,197
60	58,500	0.4	8.5	961	160	1,121
90	45,000	0.4	8.5	893	160	1,053
150	30,000	0.4	8.5	833	160	993
30	87,000	1.0	19.1	1,967	400	2,367
150	30,000	1.0	19.1	1,643	400	2,043

* As estimated using PHOEBE code for fuel with burnup of 10,000 Mw.-days/MTU as a specific powder of 20 kw./kg. of uranium.

† Based on 125 pounds of alumina per cubic foot and 1.5 cubic feet of cladding fines per MTU.

‡ Based on cost table in IDO-14595 and calculation of annular bin thickness assuming that 90% of fission product powder in feed goes to storage and that bed centerline-to-wall ΔT is 1000°C. with a thermal conductivity of 0.3 Btu./hr.-ft.-°F.

§ Assuming cost of $0.40 per kg. of alumina.

It is also indicated that some storage cost saving may be made by processing longer cooled fuel; however, this saving apparently is not large enough to be economically controlling at the same waste volume. If processing of longer cooled fuel allowed reduction in waste volume, the economic significance would be much greater.

Finally, the cost of alumina is not a large factor for the $0.40 per kg. (or less) variety; however, one grade has been considered which would cost about $1.50 per kg. The cost differential for the more expensive alumina is certainly important at 1.0 kg. of alumina per kg. of uranium and is not insignificant at the 0.4 ratio. Nevertheless, use of the higher priced grade would well be justified if it can be employed through more recycles.

CRITICALITY CALCULATIONS

High Enrichment Fuels

One advantage of a volatility process is that the critical mass for the poorly moderated systems is high relative to that for aqueous solution

processing. Calculations were made for the purpose of estimating the critical mass for highly enriched uranium processing. The limiting case was considered to be the fully reflected sphere.

Accordingly, sizes and uranium masses for urano-uranic oxide spheres reflected with alumina or water were calculated for several values of k_{eff} from 0.9 to 1.0. The uranium-235 density was taken as 3.0 g./cc., which is felt to be the maximum conceivable value for the processes and fuels being considered. The DTK and DDK transport codes were used for the calculations. The results are given in table VI.

TABLE VI

CRITICAL SIZE OF URANO-URANIC OXIDE* SPHERES FOR DIFFERENT MULTIPLICATION FACTORS, k_{eff}

k_{eff}	Radius, cm.	Uranium-235 Mass, kg.	Reflector†
1.00	24.58	186.6	Water
0.95	22.68	146.6	Water
1.00	21.08	117.7	Alumina
0.98	20.58	109.5	Alumina
0.95	19.80	97.55	Alumina
0.90	18.60	80.86	Alumina

* Uranium is 100% uranium-235 at a density of 3.0 g./cc.

† The reflector thickness is 30 cm., with water and alumina densities of 1.0 and 2.5 g./cc., respectively.

The reflected sphere at 3.0 g./cc. uranium-235 density has been taken as the controlling case, since spheres or cylinders of lower uranium density have somewhat higher critical masses. The possibility of obtaining a sphere or sphere-like geometry with the assumed uranium density is thought to be very slim; accordingly, this assumption is probably quite conservative.

The results also indicate that, for the large reflector thicknesses used, spheres have somewhat lower masses for the same k_{eff} for alumina reflection than for water reflection. Usually, the equivalent of the water-reflected situation might be expected to hold; however, pending analysis of possible effective reflection by furnace and vessel components, as well as alumina contained in the process vessels, the more restrictive alumina-reflected cases are being used.

With the estimated potential calculation error of 2% in k_{eff}, the critical mass of uranium would appear to be greater than 109 kg. As the uranium-235 is diluted with uranium-238 to hold a uranium-235 density of 3.0 g./cc., the critical uranium mass will increase; however, the mass of uranium-235 required for criticality will decrease slightly.

The calculations also indicate that, for either water or alumina reflection, the neutron spectrum is quite fast. For example, at k_{eff} equal to 1, 99% of the neutrons has an energy greater than 10 KEV.

Low Enrichment Fuels

During reprocessing of low enrichment nuclear reactor fuels by fluid-bed fluoride volatility methods, large quantities of uranium dioxide will be contained in the fluid-bed reactors proposed. Several calculations were made using the DTK transport code to determine nuclear properties of uranium dioxide systems for criticality control purposes*. In order to obtain mass limits, homogeneous mixtures of materials were assumed. The ultraconservative case where minimum critical masses result from optimum spacing of feed in a matrix arrangement was not employed. Such a condition is highly unlikely here, particularly considering the relatively small size of the fuel fragments and the random arrangement implied for dumped beds.

Since processing will take place in the dry state at elevated temperatures, assumption of water moderation is unnecessarily restrictive; therefore, neutron multiplication factors in infinite media, i.e., k_∞, are listed in table VII for mixtures containing alumina granules and pellets of uranium dioxide at 2 and 5% uranium-235 enrichment.

TABLE VII

INFINITE MEDIUM NEUTRON MULTIPLICATION CONSTANTS
FOR URANIUM DIOXIDE-ALUMINA MIXTURES

Uranium Concentration, g./cc. bulk*	k_∞	
	2% Enrichment	5% Enrichment
8.814	0.551	0.843
7.051	0.538	0.828
5.289	0.552	-

* The density of alumina was assumed to be 2.5 g./cc.

Since all the k_∞'s are less than 1, a finite system containing any of the above mixtures presents no criticality problem according to the calculations.

* In the event that unirradiated or very short burnup fuels were processed, plutonium would be essentially absent; additional calculations for high burnup fuels are planned in which the largely compensatory effects of uranium-235 depletion and plutonium buildup are considered.

As just noted, elevated temperatures and the sequence of processing steps, no water in liquid form should be present in the equipment. Nevertheless, computations were made in order to evaluate the "order-of-magnitude" of limits for uranium dioxide-water systems. Infinite multiplication factors were determined for uranium dioxide concentrations between 10 and 60 volume percent. In all cases involving 2 and 5% enrichment, k_∞ was close to or greater than one.

The study was extended to include determinations of critical properties of geometric systems (cylinders and spheres) containing uranium dioxide pellets and water. The cylinder calculations assumed infinite length with 30 cm. of water reflection. Critical radii are shown in table VIII.

TABLE VIII

CRITICAL RADII OF INFINITE CYLINDERS*
CONTAINING URANIUM DIOXIDE-WATER MIXTURES

Uranium Dioxide, volume percent	Uranium Concentration, g./cc.	Critical Radius, cm.	
		2% Enrichment	5% Enrichment
60	5.765	-	29.80
40	3.843	30.91	17.61
30	2.882	25.67	15.28
20	1.992	26.59	14.11
10	0.9608	-	15.37

* Reflected with 30 cm. of water.

Table IX gives the critical masses and critical radii of several spheres containing uranium dioxide-water mixtures, assuming 30 cm. of water reflection. The minimum critical masses appear to be about 370 kg. of 2% enriched uranium at 21 volume percent uranium dioxide in water and 37 kg. of 5% enriched uranium at 9.4 volume percent uranium dioxide in water.

TABLE IX

CRITICAL SPHERES* OF URANIUM DIOXIDE-WATER MIXTURES

Uranium Dioxide, volume percent	Uranium Enrichment, Percent Uranium-235	Uranium Concentration, g./cc.	Critical Radius, cm.	Critical Mass, kg. of U
25	2	2.402	33.93	393.02
20	2	1.992	36.04	376.89
15	2	1.441	41.65	436.1
13	2	1.249	49.41	631.1
15.5	5	1.489	19.68	47.54
12	5	1.153	20.37	40.82
8	5	0.7684	22.81	38.20
6	5	0.5764	26.72	46.06

* Reflected with 30 cm. of water.

When a k_{eff} of 0.90 is employed for mixtures of uranium dioxide pellets in water, computations indicate that a sphere containing 21 volume percent uranium dioxide at 2% enrichment should be limited to a radius of 25.88 cm. The mass limit for the above set of conditions is thus 146 kg. of uranium; i.e., the amount of uranium contained in such a sphere at the optimum hydrogen-to-uranium ratio. Likewise, a sphere with 9.4 volume percent uranium dioxide at 5% enrichment should have a radius of 17.60 cm. and a mass of 20.62 kg. of uranium.

Since these critical quantities for liquid water-uranium dioxide mixtures are less than the conceptual design point batch charge of about 500 kg. of uranium, the contemplated precautions in design and the use of operating interlocks which will, to a satisfactory degree, prevent liquid water interjection appear to be mandatory. These precautions include use of air cooling for the reactor and auxiliaries, and provision of sensor activated interlocks to prevent operation at temperatures which would allow liquid hydrogeneous material accumulation.

Plutonium

Four critical mass calculations have been made for spherical plutonium salt assemblies reflected with alumina. The resultant numbers provide some orientation for critical mass problems involved in power reactor fuel processing. Table X gives the results of these computations. At a reflector thickness of 50 cc. and a plutonium density of 4.6 g./cc., the critical radius was 10.79 cm., and the critical mass was 24.2 kg. of plutonium. The total diameter of the core reflector assembly was about 123 cm. The critical mass for the high density spheres of plutonium

dioxide is about 20% of that found for spheres of urano-uranic oxide with 3.0 grams of uranium per cubic centimeter.

TABLE X

CRITICAL MASS OF PLUTONIUM DIOXIDE SPHERES
REFLECTED WITH ALUMINA

Plutonium Density*, g./cc.	Reflector Thickness†, in.	Critical Radius, cm.	Critical Mass of Plutonium, kg.
3.0	12.8	15.14	43.6
4.6	0	17.86	109.8
4.6	12.8	11.20	27.1
4.6	20.0	10.79	24.2

* The plutonium densities of 3.0 and 4.6 g./cc. are based on 30 and 45% of the theoretical crystal density of plutonium dioxide, respectively.

† The density of alumina reflector was taken as 2.5 g./cc.

It should be realized that the assumed plutonium densities and reflector thicknesses may be unnecessarily restrictive. Additionally, it should be recognized that plutonium-239 was used for the calculation rather than the probably less reactive mixture of the 239, 240, 241, and 242 isotopes present in the irradiated low assay enriched uranium dioxide power reactor fuels.

COLD TRAPS

Final collection of uranium hexafluoride in any of the volatility processing methods will be accomplished by desublimation in a refrigerated heat exchanger; i.e., cold trap. Batch desublimers have been generally used for condensation of uranium hexafluoride as a solid since the inception of the uranium isotope separation program in the early 1940's. A design procedure* was worked out at that time which, in essence, is still being used. This procedure utilized the basic heat and mass transfer equations which were interrelated by the application of the Chilton-Colburn j-factor equations. One of the biggest difficulties was prediction of the holding capacity of a trap, since the point accumulation rates for the empty exchanger were assumed to hold to plugging without correction for the effects of the deposit or the increase in gas velocities. Experimental work on several sizes of traps of similar geometry, however, allowed formulation of empirical correction factors.

* Thompson, W. I., "Theory of Heat and Mass Transfer in Batch Condensation of Solids", Engineering Developments in the Gaseous Diffusion Process, U.S.A.E.C., Technical Information Service Extension, Oak Ridge, Tennessee, 1949 (NNES-II-16).

Because of the emerging requirements for new cold trap designs for the uranium hexafluoride and plutonium hexafluoride in volatility programs, coupled with the ready availability of high speed data processing equipment, improvements to this historic procedure are now both justified and possible. Accordingly, a desublimer design digital computer program is being developed.

A series of checks of the computer program is being made for a 10-inch diameter, "egg-crate" type trap design*. This trap is employed in the facility used for reprocessing uranium scrap returns at ORGDP. The theoretical uranium hexafluoride capacity is being calculated for various inlet concentrations of uranium hexafluoride, noncondensable flow rates, and inlet temperatures. In the future, such investigations will be of importance in the design of cold traps, not only for uranium hexafluoride, but for other desublimable materials. Availability of ready calculation techniques will potentially allow study of the basic characteristics of desublimer designs at a much lower cost than pilot plant testing.

Before such computer simulation studies can be accepted and given credence, it must, of course, be shown that the results are consistent with those observed on operating systems. Accordingly, comparison of available data from both experimental testing and production operation of various traps with corresponding calculated results is planned.

Preliminary results of calculations are shown in table XI. The estimated operating conditions for this size trap in the ORGDP scrap reprocessing area are inlet temperature, about 60°C.; flow rate, about 0.4 pound per mole inert per hour; and inlet concentration of uranium hexafluoride, about 15 mole percent. The calculated capacity for these conditions is lower than the reported operational experience of approximately 270 pounds of uranium hexafluoride, although it can be seen that calculations for somewhat lower uranium hexafluoride concentrations and somewhat higher noncondensable flow rates tend toward this figure. As with any other batch desublimation problem, assumptions made as to the thermal conductivity and, particularly, density of the deposit are relatively crucial in estimating batch capacity. Unfortunately, accurate information as to the values of these deposit characteristics for various conditions of deposition appears to be scarce.

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* Such a trap is depicted in the following reference: Smiley, S. H., Brater, D. C., Littlefield, C. C., and Pashley, J. H., "Quantitative Recovery of Uranium Hexafluoride from a Process Gas Stream", Ind. Eng. Chem., 51, 191-196 (1959).

TABLE XI

CALCULATED URANIUM HEXAFLUORIDE CAPACITY
FOR 10-INCH DIAMETER, "EGG-CRATE" TYPE COLD TRAP

Inlet Uranium Hexafluoride, mole percent	Inert Flow Rate, lb. mole/hr.	Inlet Gas Temperature, °C.	Uranium Hexafl Holding Capaci pounds
15	0.4	60	218
15	0.6	60	246
15	0.4	40	233
15	0.4	90	253
30	0.4	60	211
5	0.4	60	259

* Calculated using a nitrogen inert, trap cooling temperature of m 48°C., desublimed solid thermal conductivity of 0.1 pcu./hr.-ft.- and bulk density of 135 pounds per cubic foot.

More exact plant trap performance data will be obtained when the re cessing system is next operated. Additionally, improvements are be made to the program which should increase calculation accuracy.

PROTOTYPE TESTING AND EVALUATION

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MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES

For a commercial reprocessing facility, it may be desirable to use a single fluid-bed reactor for all types of low and high enrichment fuels. Thus, the reactor must be able to withstand the conditions for (a) the hydrogen chloride-fluorine procedure for high enrichment zircaloy and aluminum alloy fuels, (b) the hydrogen chloride-oxygen-fluorine process for low enrichment zircaloy-clad ceramic fuels, and (c) the hydrogen fluoride plus oxygen-fluorine system for stainless steel and zircaloy-clad ceramic fuels. Because of the high temperatures during oxidation, a separate system would be required for graphite-type fuels.

To evaluate various materials, tests are being conducted in a bench-scale controlled-atmosphere loop. Samples are sealed in an electrically heated vessel, and gas of the desired composition is passed through the system at a low rate. To minimize the possibility of inleakage, an all-welded system is used. Additional data are being accumulated in conjunction with filter performance evaluation in a fluid-bed system. The results of the studies completed to date are presented in table XII. For convenience, the tests are divided into two groups, i.e., filter materials and flange and reactor materials, and will not necessarily be discussed in the numerical order shown in the table. Conditions expected for the high enrichment zircaloy and the low enrichment stainless steel-clad fuels have been studied to date. Tests with alternating hydrochlorination, oxidation, and fluorination atmospheres have been started to obtain data for the low enrichment zircaloy-clad fuel recovery process.

Filter Materials

In run 1, samples of porous nickel and Monel filter materials and a porous alumina disc were subjected to cyclic exposures at 315°C. to a mixture of zirconium tetrachloride, stannous chloride, hydrogen chloride, and hydrogen, and then to a fluorination atmosphere of uranium hexafluoride, fluorine, and nitrogen. These conditions are expected when high enrichment zircaloy fuels are reprocessed. Twenty-two cycles of alternating 16-hour hydrochlorinations and 4-hour fluorinations were made. As was anticipated, no apparent attack of the alumina was noted, while the Monel sample deteriorated extensively. Microscopic examination of the nickel sample indicated that it withstood the exposure well, as there was no evidence of cracking. Flow tests showed that the permeability was acceptable for filtering purposes.

Run 2 was made to investigate further the corrosion effects of hydrogen chloride and fluorine on sintered nickel filter material. Two samples cut from a Micrometallic type-G nickel bayonet filter tube were exposed

TABLE XII

RESULTS OF CORROSION TESTS

Test No.	Materials	Total Number of Cycles	Phase I			Phase II			Corrosion Penetration*, mils/year	Corrosion Description and Remarks
			Gas Components	Exposure Temp., °C.	Total Exposure, hr.	Gas Components	Exposure Temp., °C.	Total Exposure, hr.		
1	Porous Nickel-200 Porous Monel Alundum	22	HCl, H_2, $ZrCl_4$, $SnCl_2$	315	228	F_2, N_2, UF_6	315	81		Good condition Badly contaminated No apparent attack
2	Porous Nickel-200	20	HCl, H_2	315	216	F_2, N_2	205	80		Good condition
3	Duranickel Low P Electroless Ni Plate High P Electroless Ni Plate	20	HCl, H_2	400	246	F_2, N_2	540	87		Good condition Heavily corroded Heavily corroded
4	Porous Nickel-200 Duranickel	20	HCl, H_2, $ZrCl_4$, $SnCl_2$	315	218	F_2, N_2, UF_6	200	80	 6.9	Good condition Good condition
5	Aluminum Wire Anodized Aluminum Nickel-Coated Steel Al_2O_3-Coated Steel	1	HCl, H_2	200	100					Disintegrated Disintegrated Slight weight gain Slight weight gain
6	Hastelloy-C Hastelloy-F Hastelloy-G Hastelloy-N Duranickel Nickel-200	20	HCl, H_2	400	235	F_2, N_2	540	80	477 195 90.5 48.0 8.8 1.1	Yellow, brown flakes Heavy, yellow powder Heavy, yellow powder White, brown flakes Light, white powder Light, white powder
7	Hastelloy-C Hastelloy-F Hastelloy-G Hastelloy-N HyMu-80 Duranickel	10	HF, O_2	590	95	F_2, N_2	540	40	 1,970 238 376 117 39	Entirely consumed Heavy, yellow flakes Heavy, yellow powder Light, yellow scale Light, yellow powder Light, white powder

TABLE XII (Contd.)

RESULTS OF CORROSION TESTS

Test No.	Materials	Total Number of Cycles	Phase I			Phase II			Corrosion Penetration*, mils/year	Corrosion Description and Remarks
			Gas Components	Exposure Temp., °C.	Total Exposure, hr.	Gas Components	Exposure Temp., °C.	Total Exposure, hr.		
8	INCO-61 Rod	20	HCl, H_2	400	236	F_2, N_2	540	77	182	Yellow powder
	Silver Solder									Entirely consumed
	Welded Inconel								79.3	Heavy, yellow powder
	Inconel								55	Heavy, yellow powder
	Welded HyMu-80								41	Heavy, yellow powder
	HyMu-80								21	Heavy, yellow powder
	Welded Nickel-200								7.1	Light, yellow powder
	Nickel-200								5.1	Light, yellow powder
	Welded Nickel-201								4.9	Light, yellow powder
	Nickel-201								4.2	Light, yellow powder
	Welded Duranickel								8.2	Light, white powder
9	Porous Nickel	1				F_2, N_2	550	12		Material was heavily corroded and brittle
10	Porous Nickel	1				F_2, N_2	550	21		Material was heavily corroded and brittle

* Based on weight change and sample surface area.

alternately to hydrogen chloride in hydrogen at 315°C. and to dilute fluorine at 205°C. for twenty cycles involving 80 hours of fluorination and 216 hours of hydrochlorination. The experiment was started with a fluorination cycle and was concluded after a hydrochlorination cycle. One of the porous nickel samples was subsequently fluorinated for 4 hours before analyses were made.

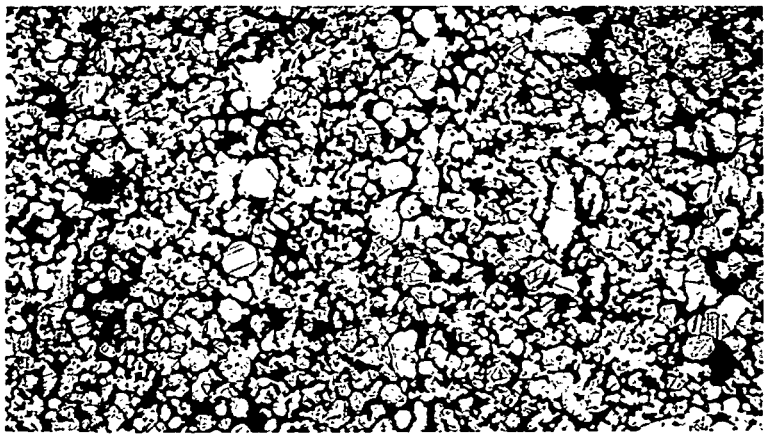
Visual inspection showed that both samples had darkened in color with a thin, reddish deposit on the bayonet weld area. Laboratory analysis of the sintered nickel showed 81 ppm. fluoride and 398 ppm. chloride after hydrochlorination and 1,170 ppm. fluoride and 130 ppm. chloride after fluorination. These low fluoride and chloride values were considered acceptable for fluoride volatility applications. Flow measurements indicated a 20% plug of the material caused by the exposure treatment, but this loss is not considered serious. Figure 5 shows the grain structures of the exposed and unexposed samples involved in this test.

A qualitative spectrographic analysis of the reddish deposit on the areas and also of the weld material itself showed unexpectedly high concentrations of iron and manganese. Modification of vendor welding procedures may be necessary if this type filter is to be used.

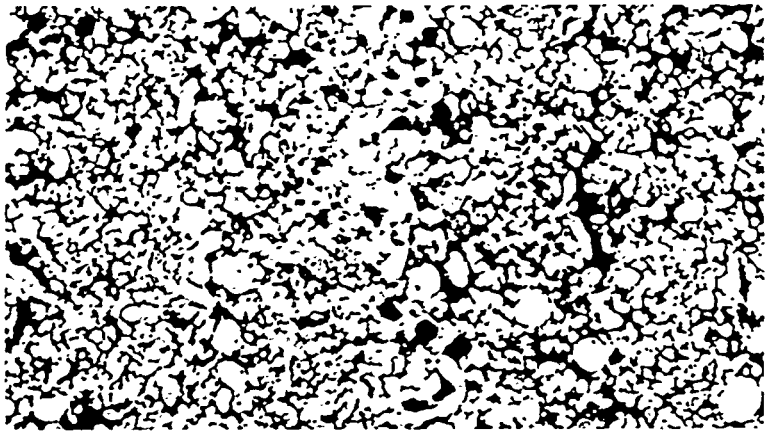
Another study of the Micrometallic type-G porous nickel material was made in test 4 wherein samples were subjected to twenty cycles of exposures to hydrogen chloride, hydrogen, and zirconium tetrachloride at 315°C. and to fluorine, uranium hexafluoride, and nitrogen at 200°C. Small weight gains of less than 1% were experienced during this test, and again the sample appeared undamaged.

It was thought originally that, in a low enrichment fuel reprocessing facility, treatment of the fluoride volatility equipment periodically with fluorine at 550°C. might be necessary to convert any reduced plutonium tetrafluoride in the system back to plutonium hexafluoride. One of the concerns of such a procedure was the effect of the treatment on the porous nickel filters. In test 9, two samples of Micrometallic porous nickel were exposed to fluorine at 550°C., one for 12 hours and one for 21 hours. Examination of the exposed materials, figure 6, showed that both samples were heavily corroded, had become very brittle, and were not acceptable as filter material. The present opinion of Argonne National Laboratory personnel is that the plutonium cleanup will be satisfactory at 350°C.; therefore, the test is to be repeated at that temperature level.

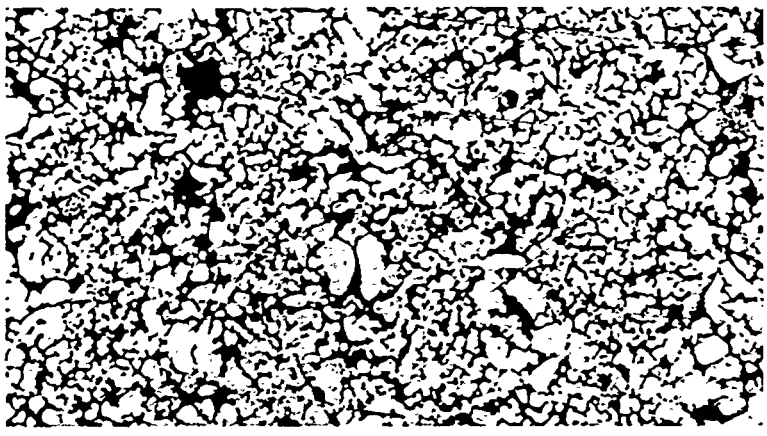
A problem which might be encountered in fluorinating a filter is that uranium deposits could react rapidly resulting in high localized temperatures and filter failure. Prediction of the magnitude of such a problem is difficult; however, it should be noted that, in a low enrichment zircaloy-clad fuel system using simultaneous oxidation and fluorination, uranium dusts should not reach the filter. Uranium accumulation on the filter would be expected with the present flow sheets for high enrichment alloy fuels and low enrichment stainless steel-clad fuels. Temperature measurements on the filter may be necessary to evaluate this



Unexposed

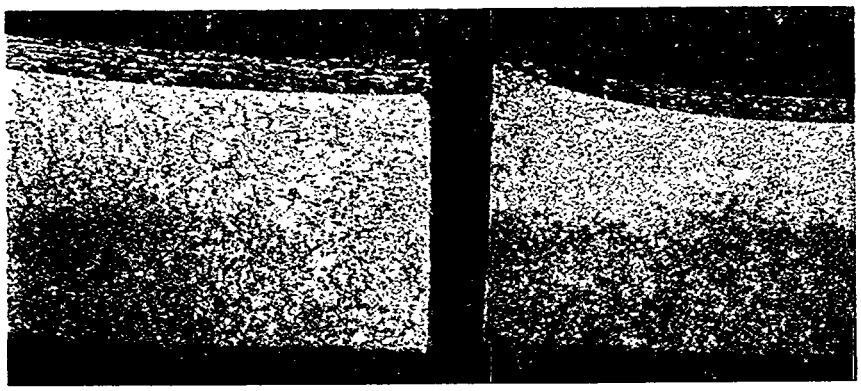


After Final HCl Treatment



After Final F_2 Treatment

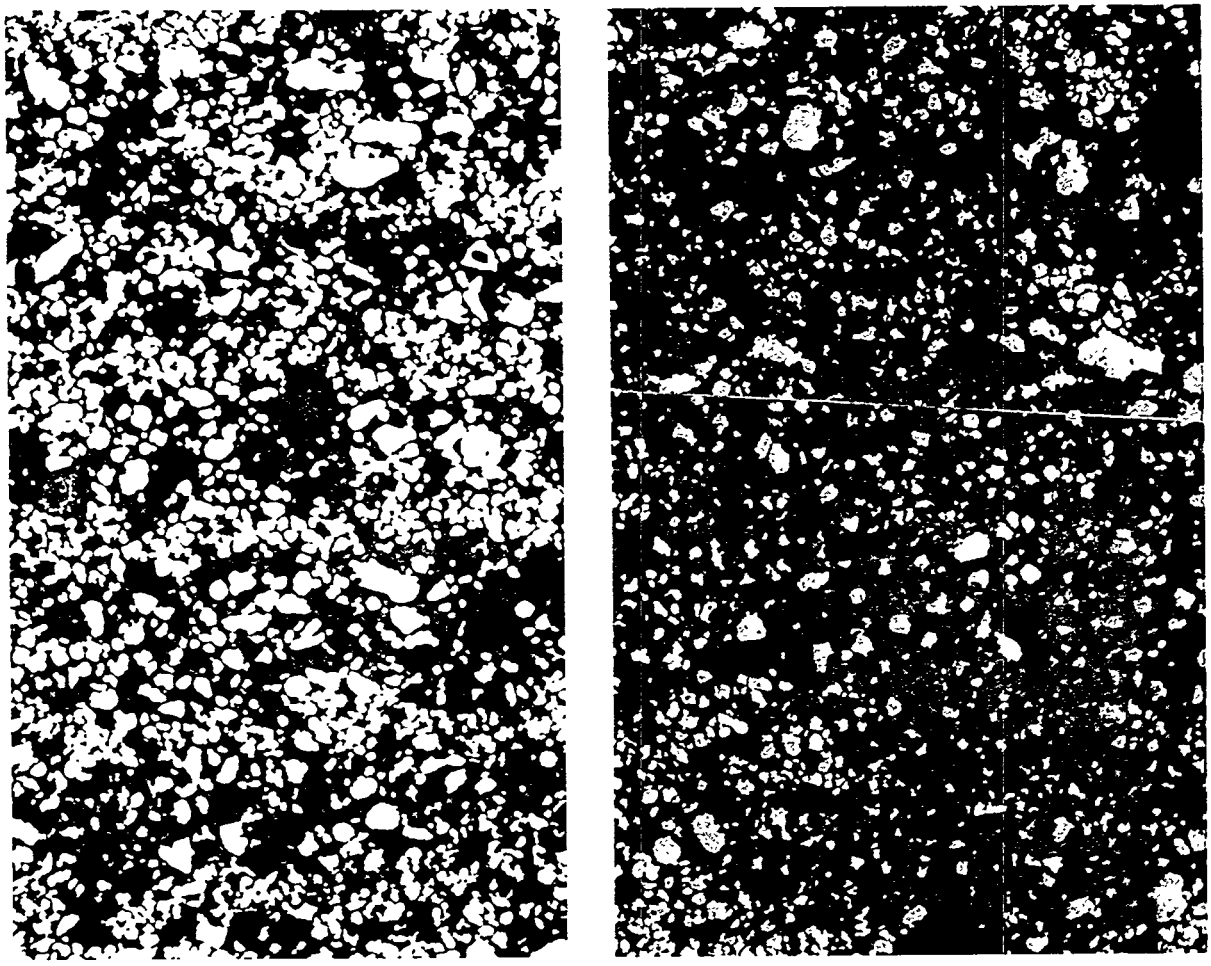
Figure 5
CORROSION OF POROUS NICKEL



21 Hours Exposure

12 Hours Exposure

1-1/4 X Magnification



12 Hours Exposure

21 Hours Exposure

50 X Magnification

Figure 6

POROUS NICKEL EXPOSED TO FLUORINE AT 550°C.

problem.

One test was also made early in the program (not shown in table XII) to investigate the suitability of various filter materials for alternating oxygen-fluorine exposures, both at 315°C. These atmospheres would be encountered in a volatility system for reprocessing graphite-type fuels. Sintered nickel, porous alumina, fine nickel wire, and nickel wool all appeared satisfactory.

Flange and Reactor Materials

The search for a hard surface for gasket compression in connector design for the process was the reason for test 3. Samples of Duranickel (a nickel alloy containing about 4-1/2% aluminum), low phosphorus electroless nickel plate, and high phosphorus electroless nickel plate were subjected to cyclic exposures of hydrogen chloride in hydrogen at 400°C. and dilute fluorine at 540°C. Twenty cycles were completed involving 246 hours of hydrochlorination and 87 hours of fluorination.

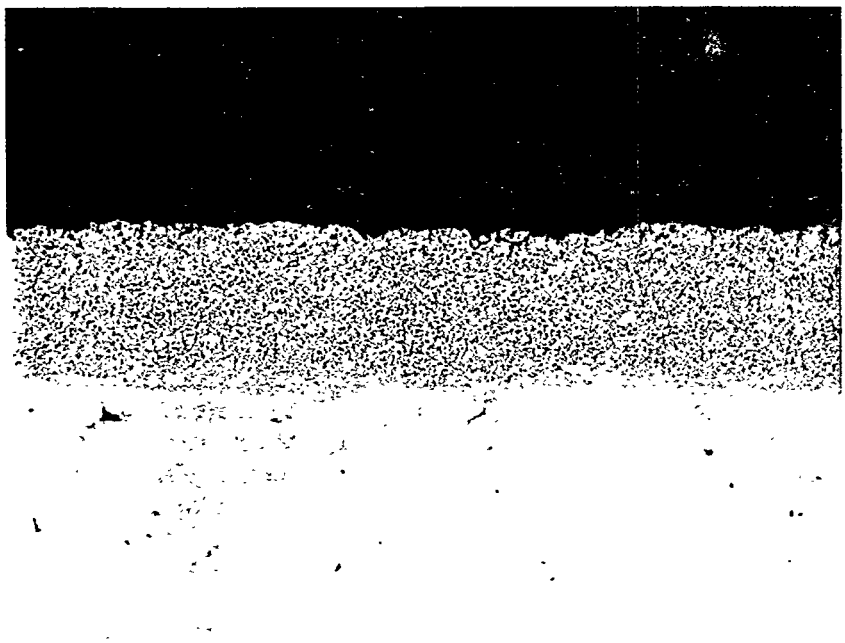
Both of the electroless nickel plate samples became heavily corroded; thick, powdery deposits formed on the surfaces. Microphotographs, figure 7, revealed that, while a considerable amount of the electroless plate remained after the exposure treatment, there was corrosion penetration into the plate.

The Duranickel sample withstood the corrosion attack well. A very light, white, powdery film was visible on the surface after exposure, and microphotographs, figure 8, showed a slight surface attack but no intergranular attack. These results were supported in subsequent tests, 4, 6, and 8, which indicate a corrosion rate of less than 10 mils per year under similar exposure conditions.

In test 5, parts of a proposed canned rotor pump having possible application for gas recycle during fuel reprocessing was subjected to a flow of hydrogen chloride in hydrogen at 200°C. for 100 hours. As expected, samples of aluminum and anodized aluminum disintegrated. Steel and electroless nickel-plated steel parts darkened in color, but very little weight change was noted. Electroless nickel-plated steel plasma-coated with aluminum oxide appeared unaffected.

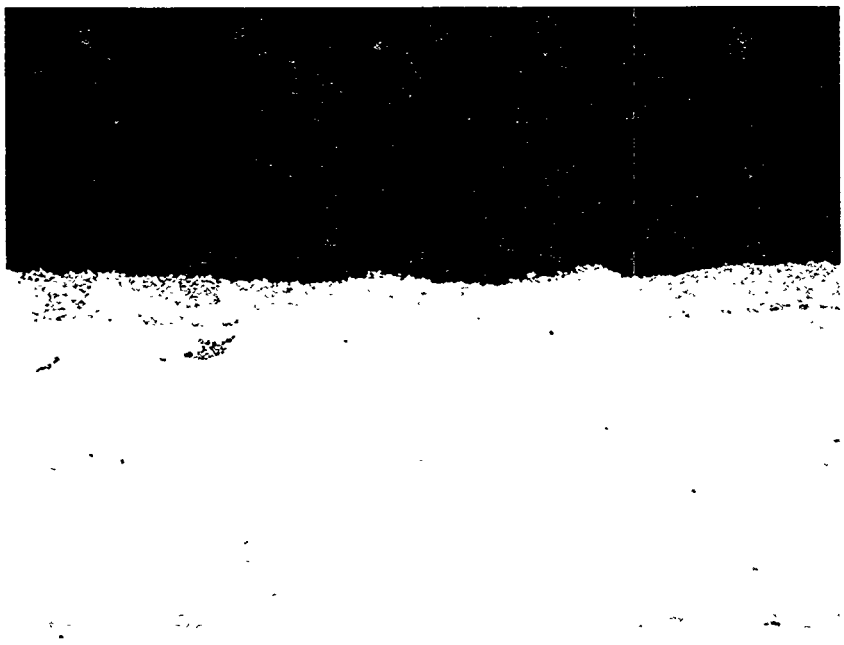
Tests 6 and 8 were made to evaluate possible materials of construction for the head-end fluid-bed reactor where high strength at elevated temperatures is required in addition to corrosion resistance. In test 6, samples of Hastelloy-C, Hastelloy-F, Hastelloy-G, Hastelloy-N, Duranickel, and nickel-200 were exposed to cyclic hydrochlorination at 400°C. and fluorination at 540°C. The corrosion penetration of the Hastelloys was found to be high compared with Duranickel and nickel-200 under the conditions of the test.

In test 8, samples of silver solder, INCO-61 welding rod, welded and unwelded Inconel, HyMu-80 (80% nickel, 4% molybdenum, and 16% iron), nickel-200, and nickel-201 were subjected to twenty cycles of alternating



Magnification 500 X

High Phosphorus

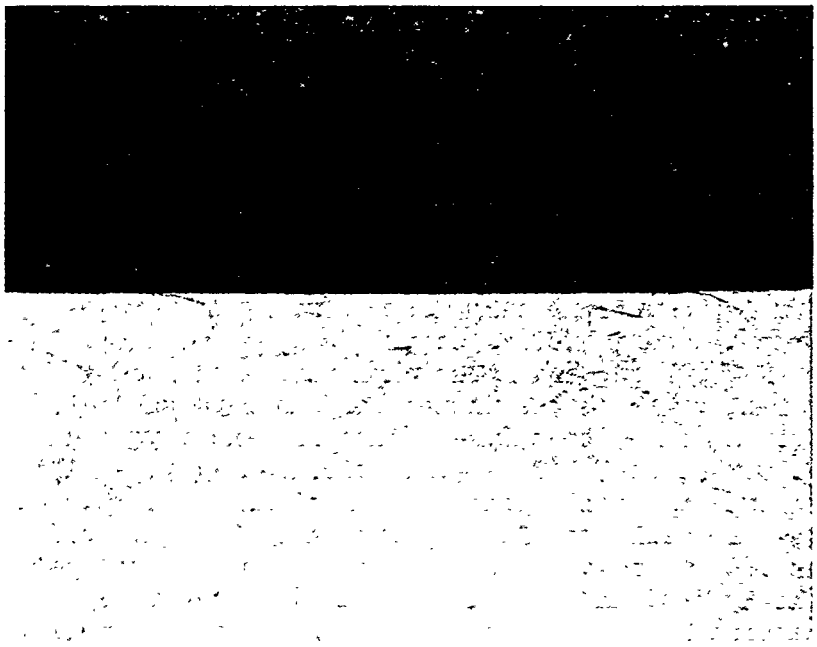


Magnification 500 X

Low Phosphorus

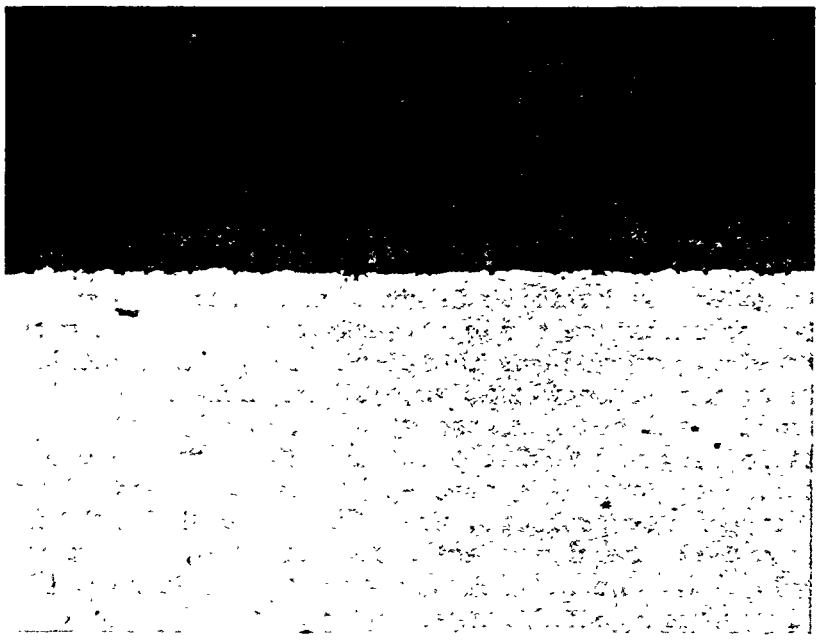
Figure 7

ELECTROLESS NICKEL PLATE CORROSION ATTACK



Magnification 500 X

Unexposed



Magnification 500 X

Exposed

Figure 8

DURANICKEL CORROSION ATTACK

exposures to hydrogen chloride and hydrogen at 400°C. and to dilute fluorine at 540°C. All nickel welds were made with INCO-61 rod, while the Inconel and HyMu-80 samples were welded with INCO-82T rod. Nickel again exhibited the best corrosion resistance. The weight losses for the welded samples were greater than those for unwelded samples of the same materials, and microscopic inspection showed the corrosion penetration of the weld material to be several times that of the base metal. Some of the samples after exposure are illustrated in figures 9 and 10.

Stainless steel-clad fuel elements require decladding in a hydrogen fluoride-oxygen atmosphere; therefore, in test 7, samples of Hastelloy-C, Hastelloy-G, Hastelloy-N, HyMu-80, and Duranickel were suspended in the filter loop fluid-bed reactor above the powder bed and were subjected to ten cycles of alternate exposures to hydrogen fluoride and oxygen at 590°C. and to dilute fluorine at 540°C. Again, the Hastelloys exhibited poor resistance to the exposure conditions. The Hastelloy-C sample corroded to the extent that it fell from its support into the fluid bed during the sixth cycle and was assumed to be consumed during the test. Microphotographs of the HyMu-80 and Hastelloy-N samples, figure 11, show the attack on these materials. While Duranickel exhibited fair resistance to corrosion, based on penetration data, some intergranular attack was present, as shown in figure 12.

In summary, it is apparent that nickel-200, nickel-201, and Duranickel are the most corrosion-resistant materials tested to date. As new alloys become available, they will be exposed to similar conditions; e.g., samples of an alloy called Berylco Nickel-440 are being prepared for testing. This metal contains small quantities of beryllium and titanium and has age hardening properties which might be useful in flange face application.

PROCESS AND REACTOR STUDIES

Extension of studies made at the National Laboratories will be necessary to prove the volatility processes on a larger scale and to obtain good engineering design data for a production facility. The major uncertainty in basing plant design on the present small-scale work arises from the fact that good fluidization and bed homogeneity are probably not achieved during the decladding and pellet oxidation steps for recovery of low enrichment zircaloy or stainless steel-clad fuels. Predictions of heat transfer and gas contact problems, therefore, are difficult if not impossible. To obtain the required design information, process work on a larger scale is planned. The initial tests will be made in a 10-inch diameter head end reactor. Still larger equipment will be used if necessary. In addition, the decladding and fluorination reactions will be observed in the filter test loop in conjunction with that test program. Inert gas fluidization will also be studied in transparent columns to evaluate proposed reactor sizing and configuration.

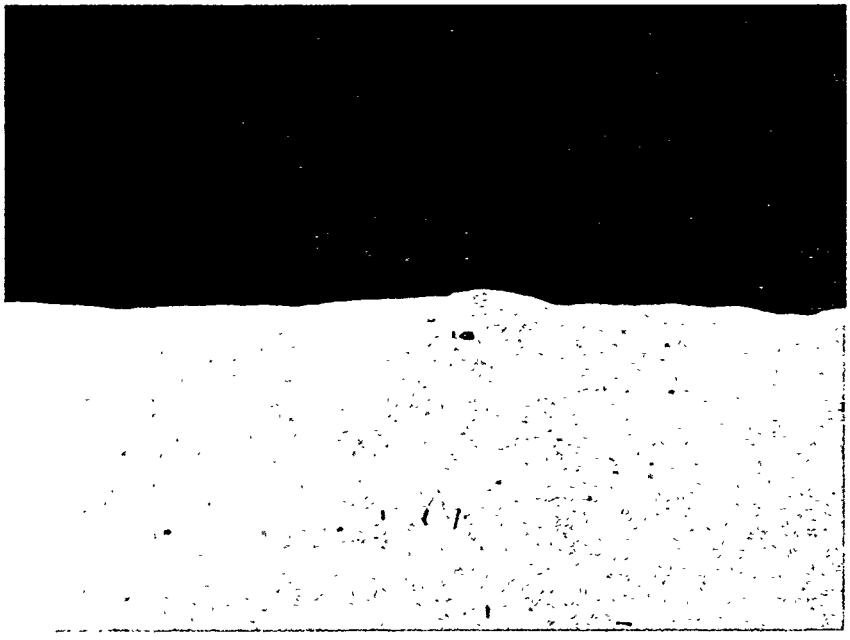
Plastic

Corrosion

Hy Mu-80

Magnification 500 X

Hy Mu-80



Plastic

Corrosion

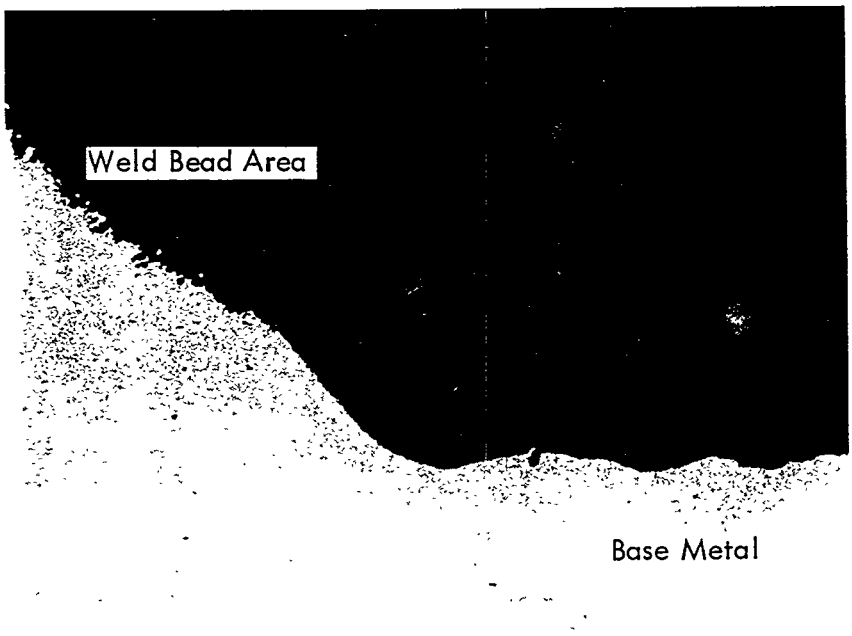
Hastelloy N

Magnification 500 X

Hastelloy N

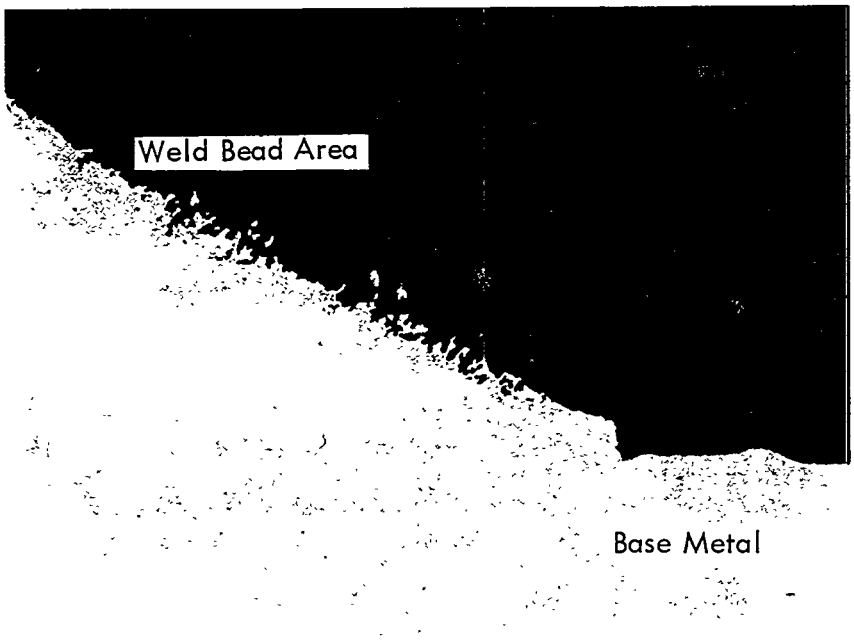
Figure 9

CORROSION RESULTS (TEST #8)



Magnification 250 X

Ni-200



Magnification 250 X

Ni-201

Figure 10
CORROSION RESULTS (TEST #8)

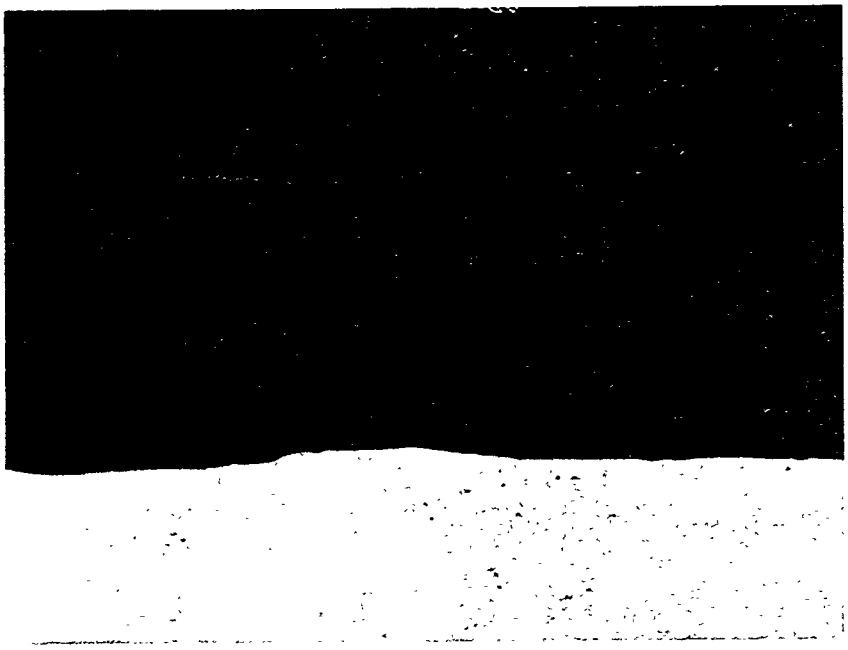
Plastic

Corrosion

Hy Mu-80

Magnification 500 X

Hy Mu-80



Plastic

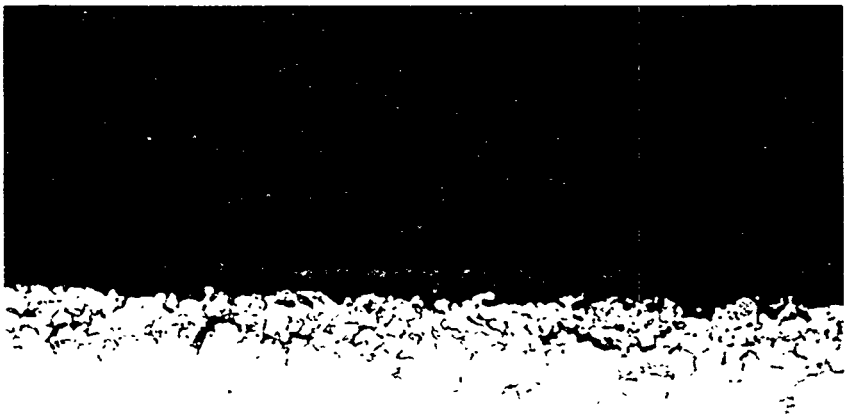
Corrosion

Hastelloy N

Magnification 500 X

Hastelloy N

Figure 11
CORROSION RESULTS (TEST #7)



Magnification 500 X

Duranickel

Figure 12
CORROSION RESULTS (TEST #7)

Decladding and Fluorination Studies

Some studies related to the hydrogen chloride reaction with high enrichment zirconium alloy fuels have been made in conjunction with filter tests which are described later. In these studies, where expected conditions at the filter must be simulated as nearly as possible, information on the performance of the fluid-bed reactor for the various process steps is generated at little or no additional cost. Uranium metal was added to the fluid bed before halogenation to simulate more nearly conditions which might increase filter loading, either from volatile uranium tetrachloride or from fine uranium trichloride particulates. Inspection following hydrochlorination showed that the bed was black instead of the green uranium chloride color expected. Analyses of the bed material detected the presence of uranium dioxide.

Although the formation of uranium dioxide was unexpected, it is known that uranium will react readily with oxygen and even preferentially in basically chloride systems; therefore, a series of test runs was conducted to determine the oxygen source. The tests included (a) substituting magnesium fluoride as a fluid-bed media instead of alumina, (b) drying the hydrogen with Molecular Sieves, (c) drying the hydrogen chloride with refrigerated silica gel, and (d) substituting argon for the nitrogen diluent. In all cases, oxidation of the uranium still occurred, thus indicating that the oxygen contents of the nitrogen and argon diluents were higher than could be tolerated. This assumption was verified when a test run made with undiluted hydrogen and hydrogen chloride gave a green reaction product in the bed.

During the testing of sintered Monel filters in the hydrogen fluoride-oxygen system proposed for decladding stainless steel-clad uranium dioxide fuel elements, a number of observations relating to performance of the fluid bed were made. Several test decladding runs were made using stainless steel 347 and 304L tubing. Hydrogen fluoride concentrations were varied from 15 to 80%, and reaction temperatures covered a wide range of 540 to 620°C. In general, the observations reported by ANL and BNL were verified. A hydrogen fluoride concentration of 40% and a bed temperature of 590°C. appeared to be the optimum. In all cases, the decladding reaction produced a hard, coarse oxide scale that was slightly magnetic and insoluble in hydrochloric acid. Fluorination treatment broke the scale into fine particles.

Presently, studies of pulverizing uranium dioxide pellets by oxidation and of fluorinating the resulting urano-uranic oxide to uranium hexafluoride are being made in conjunction with Purolater filter unit tests.

Inert Gas Fluidization

Two brief investigations were made with fluid beds utilizing glass columns for visual observation. The first of these was carried out to determine the possibility of simplifying low enrichment stainless steel clad fuel reprocessing by separating the stainless steel oxide scale from the alumina bed by elutriation. The bench-scale unit consisted of

a 2-inch diameter glass column mounted below a 5-inch diameter glass column. Air for fluidizing and elutriation entered at the bottom of the 2-inch column. The columns were filled with minus 100-mesh tabular alumina to a height of about 6 inches in the 5-inch column, and 500 grams of coarse stainless steel oxide scale was inserted on the top of this bed.

When an air flow was established, the stainless scale moved downward through the two glass sections and collected in the 2-inch portion; however, complete separation could not be accomplished with gas velocities as great as 10 feet per second. A velocity of 20 feet per second in the 2-inch column elutriated both the alumina and the scale.

In a second test, the 5-inch glass column was used to observe fluidization in a simulated bed of uranium dioxide pellets. The conical bottom was filled with 1/2- and 1/4-inch steel balls. Minus 60-mesh tabular alumina was then added to the column to a depth of 1 foot. This bed fluidized nicely at a gas velocity of 0.2 to 0.6 foot per second, and some elutriation was evident at about 1 foot per second. Stainless steel pellets, 1/2 inch in diameter by 1 inch long (simulating oxide fuel pellets), were then inserted on top of the alumina bed to a depth of 4 to 5 inches. The pellets moved downward through the bed during fluidization to the ball bearing base; however, movement around the pellets was essentially nil even with gas velocities as high as 3 feet per second. Some evidence of gas channeling through the pellets was observed.

The test was repeated using 60- to 100-mesh Norton RR Alundum. Although a higher fluidization velocity was required (0.75 to 1.0 foot per second), the results were essentially the same as with tabular alumina.

An 8-inch transparent plastic column is being fabricated to study fluidization and gas flows in beds containing simulated reactor fuel modules.

Semiworks Reactor

The design of the planned semiworks head-end reactor is shown in figure 13. The 10-inch diameter reactor will be provided with a 3-1/2-foot long, 5-inch diameter lower section for the initial tests. The reduction in diameter at the bottom of the reactor will increase the gas velocity through the portion of the bed which will contain the nonfluidizable chunks of stainless steel oxides and/or uranium dioxide pellets. Improved heat transfer and gas contact should result. If the two-diameter concept proves to be undesirable, this lower section can be removed easily. Furthermore, bottom sections of different dimensions can be fabricated and evaluated if program results indicate the expediency of such an approach.

The reactor dimensions are almost half those estimated for a production unit capable of processing about 500 kg. of uranium dioxide per batch. A charge of 65 to 85 kg. of uranium dioxide will be used. Studies of both the hydrogen chloride and hydrogen fluoride-oxygen decladding methods will be possible, and fluorine introduction will be provided at several

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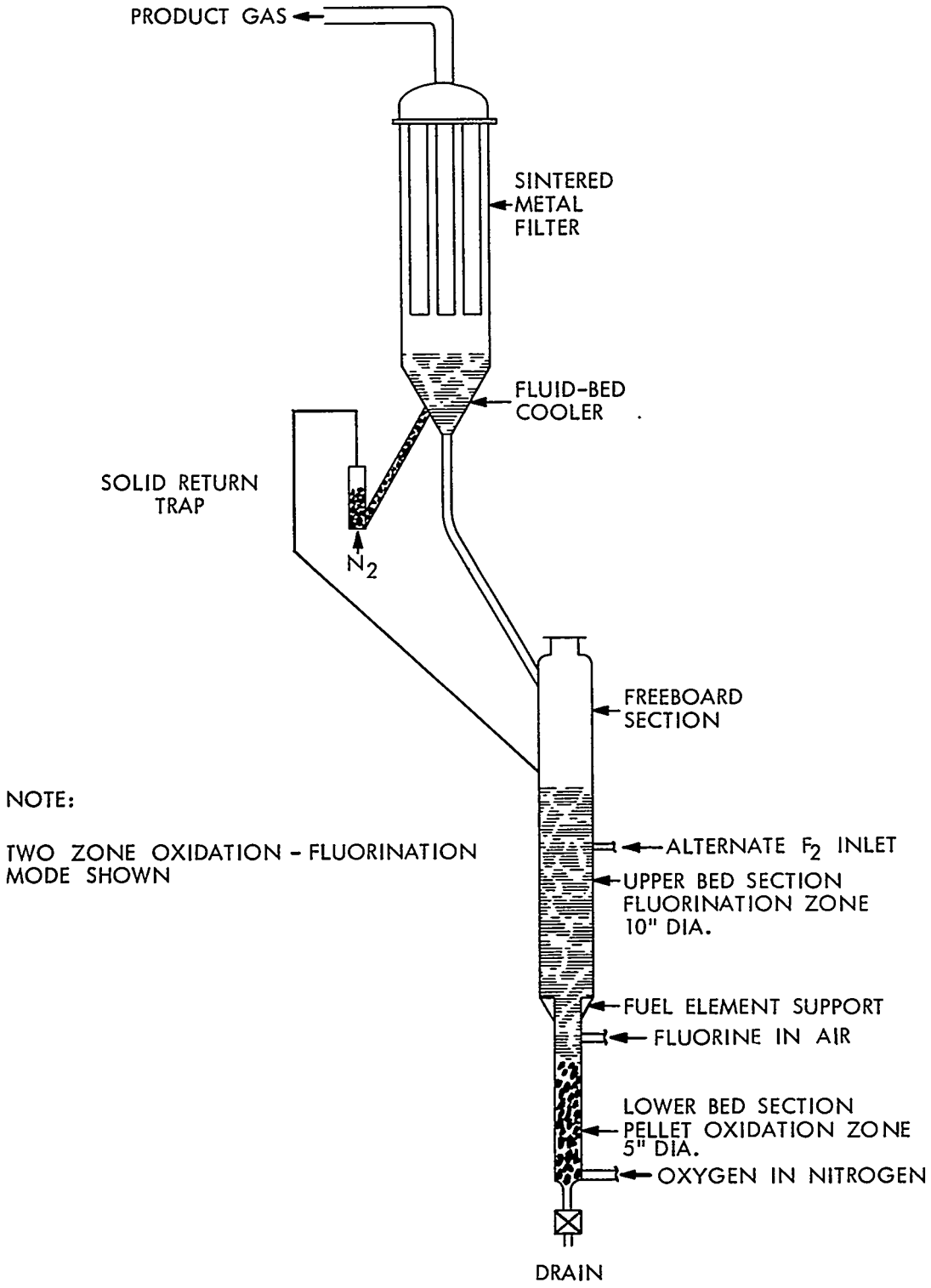

Figure 13

SEMI-WORKS FLUID-BED REACTOR

points so that simultaneous oxidation and fluorination can be evaluated. The system could also be modified to test the bromine pentafluoride fluorination flow sheet.

Based on an anticipated specific reaction rate of 34 kg. of uranium hexafluoride per hour per square foot of cross-sectional area, about 20 kg. of uranium hexafluoride will be produced per hour in the 10-inch diameter bed with a heat generation of about 50,000 Btu./hr. Setting the bed depth at 5 feet, the heat flux at the inside wall is about 3,800 Btu./hr.-sq.ft. which should be removed easily, since the high temperatures of the operation, 400 to 500°C., allow a correspondingly high temperature differential between reactor and coolant.

The rate of oxidation of the uranium dioxide is expected to be stoichiometrically equivalent to the rate at which urano-uranic oxide is fluorinated; therefore, the oxidation rate of the uranium dioxide pellets will be about 34 pounds of urano-uranic oxide reacted per hour with an associated heat generation of 5,600 Btu./hr. Using a 3-foot packed bed depth in the oxidation section, the average heat flux at the inside wall is about 1,400 Btu./hr.-sq.ft. The point heat release rate is expected to be somewhat greater owing to the difficulty of achieving good fluidization and corresponding evening of temperatures in the pellet zone. Despite this factor, the high temperature differential attainable, coupled with the ability to vary the oxygen content of the feed gas, hopefully will allow reasonable control.

Off-gases from the reactor will be cooled to 100°C., probably in a fluid-bed cooler, and will be filtered through sintered nickel filter tubes. Cooling to 100°C. is specified, since in the end application, such a temperature limit is expected to minimize thermal decomposition of the plutonium hexafluoride. From a filter life standpoint, cooling to 200°C. should be ample. The product uranium hexafluoride will be collected in cold traps for accountability purposes.

For stainless steel-clad fuels, the declad procedure of present choice is hydrogen fluoride-oxygen treatment at about 600°C. Although this treatment breaks up the uranium dioxide itself into fine powder, it leaves much of the clad in the form of relatively coarse, i.e., greater than 20 mesh, shards which tend to sink to the bottom of the fluid bed. The ability to use a high gas velocity and to control reagent concentrations in the smaller diameter section of the semiworks bed should be of advantage in minimizing hot spots by control of the reaction of these pieces.

OUTLET GAS FILTER STUDIES

Commercially available sintered metal filters are being evaluated in the test loop shown in figure 14. The loop includes a 4-inch diameter fluid bed, an inlet gas preheater, an internally finned outlet gas cooler, and a filter section. The purpose of this work is to determine if sintered metal filters mounted directly above the fluid bed will give satisfactory service in the proposed volatility processes. Packed bed filters scaled

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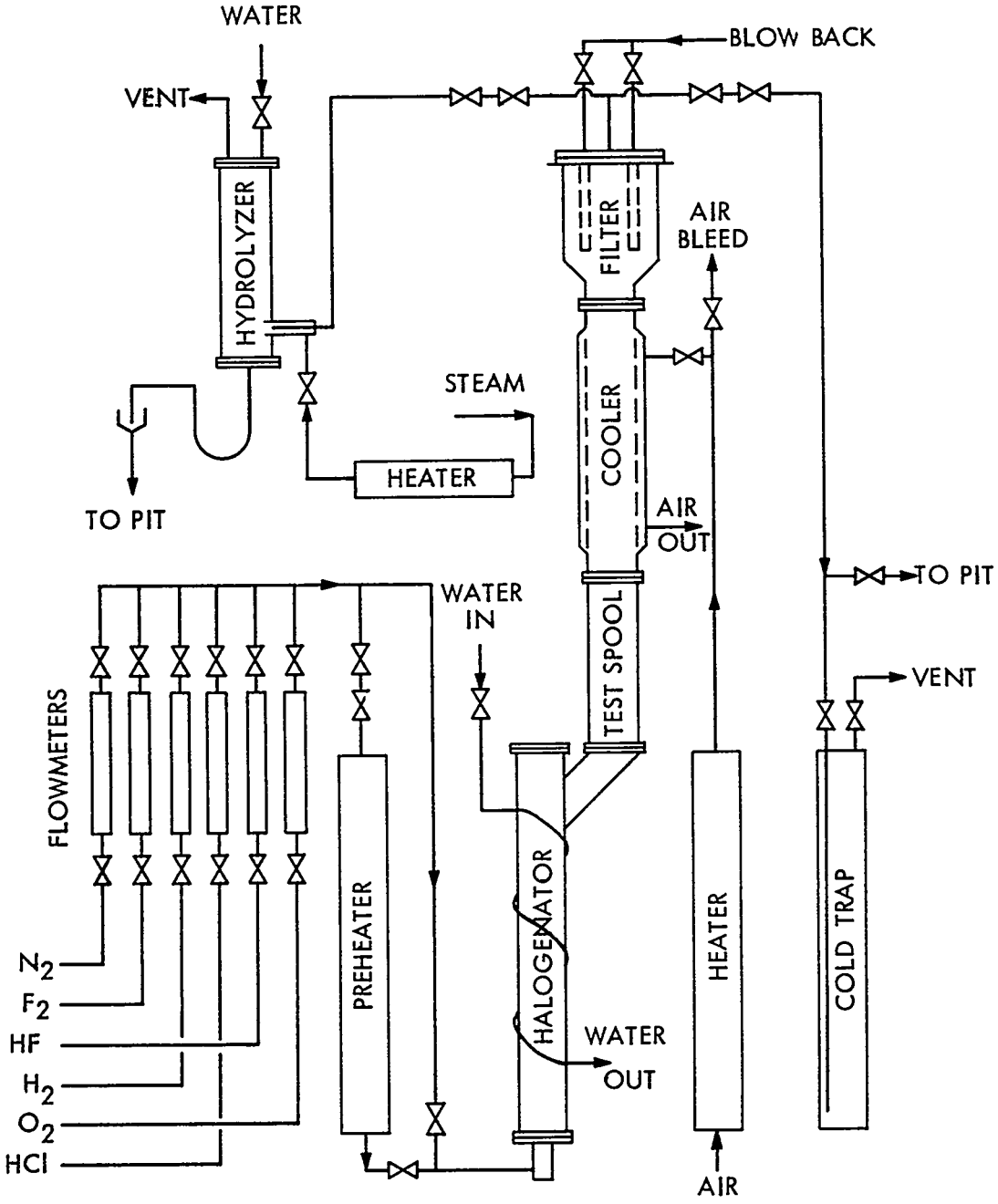

Figure 14

FILTER TEST LOOP

from laboratory studies would be quite large in a plant system and would increase the possibility of uranium and/or plutonium holdup and loss. Also, since a considerable amount of uranium dust would probably be transported to the filter during decladding and/or pellet oxidation, generation of heat at the filter during fluorination could present difficulties.

The first series of tests was made with type-G Micrometallic nickel bayonet filter tubes. During hydrofluorination, an operating temperature of 315°C. at the filter was selected because this is the minimum safe temperature necessary to prevent condensation of stannous chloride. At the flow sheet fluorination conditions, condensation will not be a problem provided the temperature is above 100°C. Based on past ORGDP experience, a maximum filter temperature of 200°C. was chosen for the fluorination step.

Two 3-inch wide by 3-foot long filter tubes were subjected to fourteen cycles in which first dilute hydrogen chloride-hydrogen and then fluorine-nitrogen mixtures were passed through a bed of Alcoa T-61 tabular alumina and through the filters. Fluidizing velocities were varied from 0.5 to 2.0 feet per second, and fluid-bed temperatures were 400°C. for the hydrochlorination step and 540°C. during fluorination. Filter temperatures were maintained at the levels noted earlier.

During the 183 hours of hydrochlorination and 56 hours of fluorination, the performance of the filters appeared normal. The pressure drop across the tubes increased rapidly and then leveled out at an acceptable value requiring only infrequent blowback. Inspection of the tubes after the runs showed a coating of fine powder which was primarily alumina containing some aluminum fluoride and nickel fluoride. Measurements on the two tubes showed air flows of 7.6 and 6.6 std. cfm., with a pressure differential of 1 psi., as compared with a flow of 28.5 std. cfm. for a new tube. Such initial plugging was anticipated. Similar results were obtained in a second series of tests during which 157 hours of hydrochlorination and 23 hours of fluorination were accumulated. In the latter test, uranium metal turnings were added to the bed before each cycle to provide uranium hexafluoride in the gas passing through the filter during fluorination.

Slight cracking at the welds of the bayonet tubes was noted after the tests just described, and the next evaluations were made with Micrometallic cylindrical tubes of the same material. After 150 hours of hydrochlorination and 20 hours of fluorination, the cylindrical tubes were inspected and were found to be badly cracked on each side of the longitudinal weld, figure 15. Analyses of the weld material showed some titanium, about 1%, indicating that INCO nickel-61 welding rod had been used.

In view of the weld cracking problems, molded (seamless) nickel filter tubes manufactured by the Purolator Corporation were obtained and are being evaluated. In these tests, an oxygen exposure has been added after hydrochlorination to simulate more nearly the process for low enrichment fuels. The exposure treatment consists of hydrogen chloride and hydrogen

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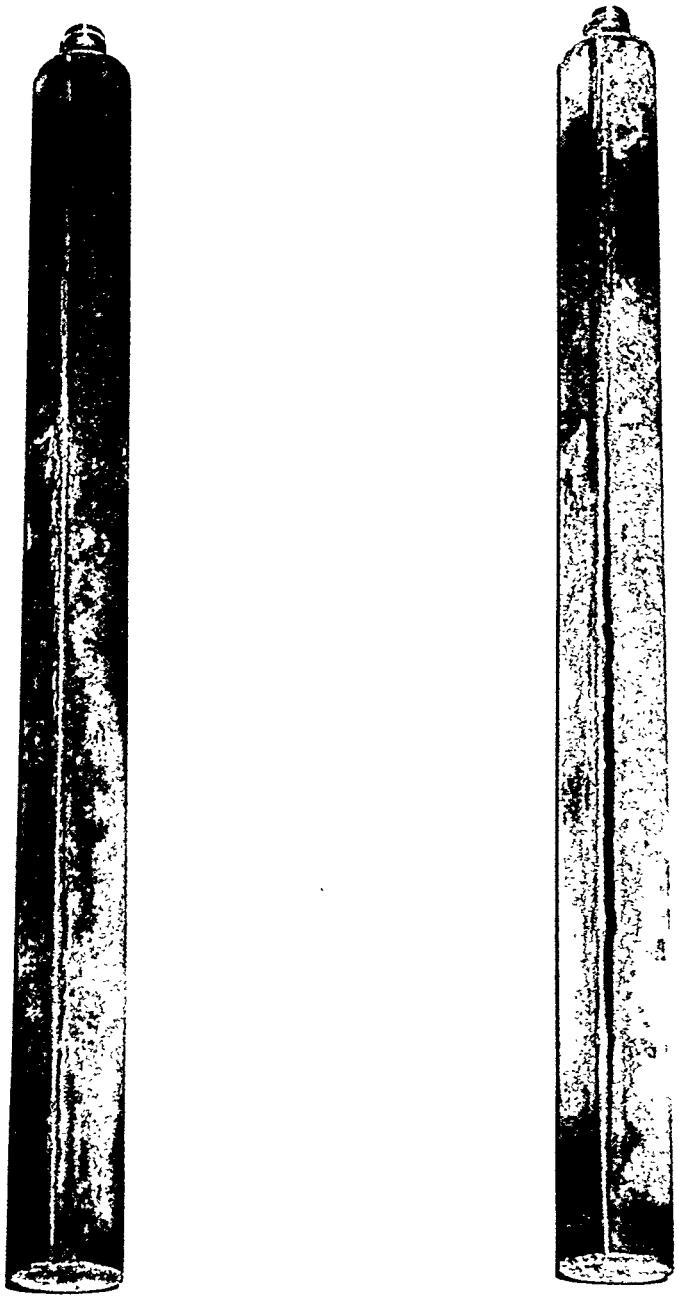

Figure 15
POROUS NICKEL FILTER FAILURES

for 5 hours at 315°C., oxygen for 10 hours at 100°C., and fluorine for 10 hours at 100°C. At the recommendation of Argonne National Laboratory, the filter temperature during fluorination was lowered from 200 to 100°C., the temperature necessary to lower plutonium decomposition to an acceptable value during actual processing. The bed in the reactor consists of minus 60-mesh tabular alumina. After four cycles, the tubes were inspected and were found to be in excellent condition. Testing is continuing.

One series of tests was made to determine the suitability of cylindrical Micrometallic Monel tubes for the alternating hydrogen fluoride-oxygen and fluorine atmospheres encountered when stainless steel-clad fuels are reprocessed. As would be expected from production experience in uranium hexafluoride manufacturing plants developed and operated by Union Carbide Corporation, these tubes were in excellent condition following 10 cycles of exposure involving about 50 hours with each gas. The filter temperature was held at 200°C. Stainless steel tubing was charged to the bed before each cycle to simulate chemical conditions during decladding. Monel tubes were not tested for the hydrochlorination-fluorination system because bench-scale corrosion tests showed rapid deterioration of the Monel.

Following the tests currently in progress, use of Inconel tubes will be studied. At the lower filter temperature of 100°C. during fluorination, Inconel may be equal to, or even better than, nickel for the combined service.

PRODUCT PURIFICATION, SORPTION-DESORPTION SYSTEM

In the flow sheets for the proposed volatility processes, there are several applications for solid sorbent traps. With high enrichment fuels where the plutonium content is negligible, fluorination off-gases are passed through high temperature (400°C.) sodium fluoride pellet traps to remove some fission products. The partially purified uranium hexafluoride is then collected on low temperature (120°C.) sodium fluoride pellets allowing other impurities, such as molybdenum, to pass through. Similar uranium hexafluoride purification in the low enrichment cases might also be possible following plutonium removal.

Studies are being made in three different systems. Investigation of operating conditions and testing of various types of sodium fluoride pellets are proceeding in a simple cylindrical trap. Trap design is being evaluated by testing a prototype annular unit; and finally, a continuous uranium hexafluoride collection system involving a fluidized bed of sodium fluoride powder and a screw regenerator is being considered. A pilot-scale unit of this latter type is available from other programs.

Cylindrical Pellet Trap

The test loop, figure 16, constructed to study pellet characteristics and effects of operating conditions consists of a vertical length of 4-inch nickel pipe providing a 7-foot deep bed of pellets. The trap is electrically heated and water-cooled and is installed with a gas metering station, cold traps, and an outlet gas uranium hexafluoride detection unit.

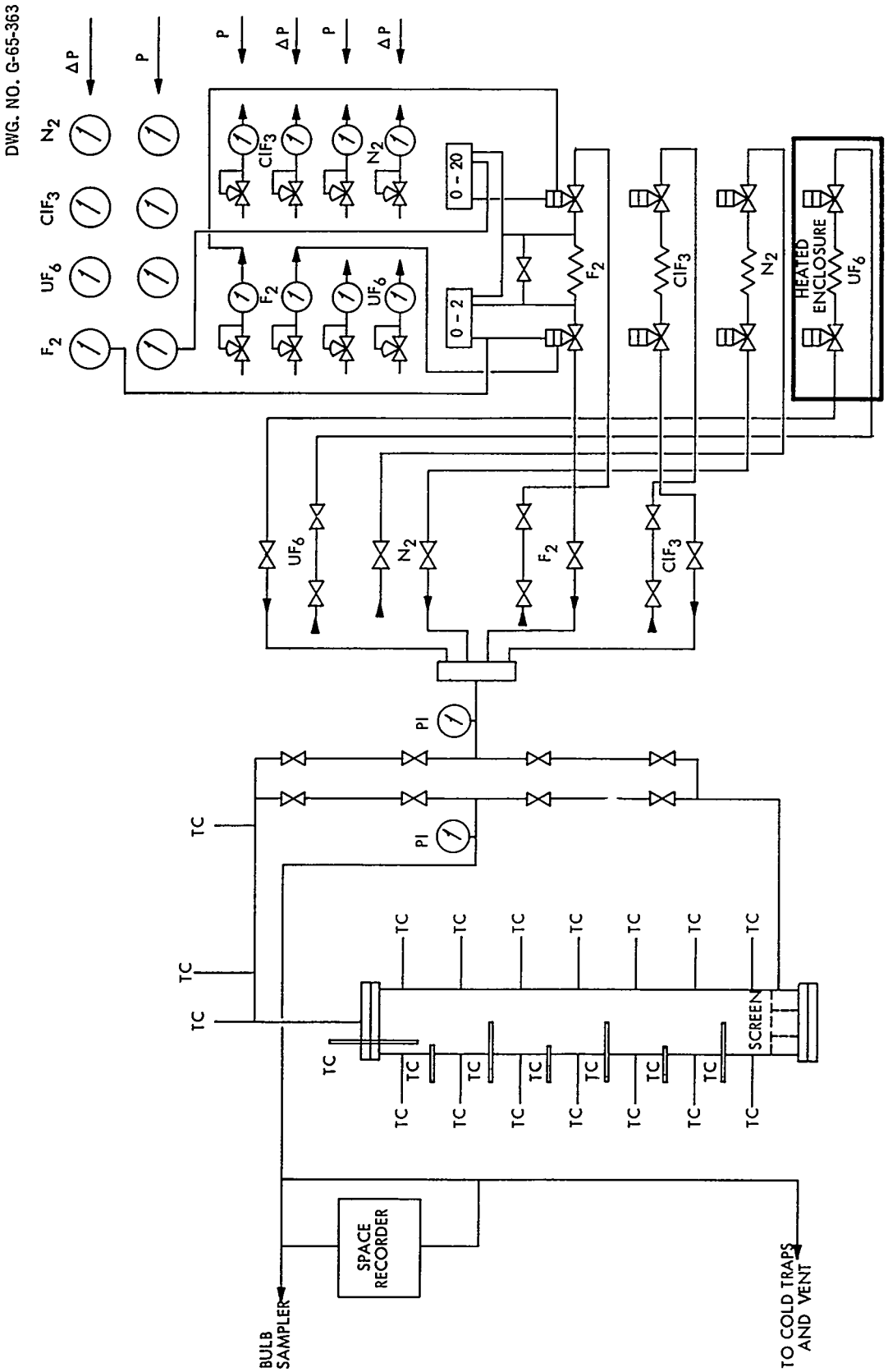

Figure 16
4" SORBER LOOP

The first series of tests, runs 1 through 24 in table XIII, was made to study the effects of various gas compositions on uranium hexafluoride sorption capability. Effects of uranium hexafluoride, fluorine, and chlorine trifluoride concentrations were determined; chlorine trifluoride will be encountered in the high enrichment process when chlorides are converted to fluorides. The sodium fluoride used was prepared from commercially available*, 1/8-inch, cylindrical pellets of sodium bifluoride by heating at 540°C. for 5 hours in an inert atmosphere. Operation was carried out using a sorption temperature of 120°C., a gas retention time of 80 seconds (assuming 100% voids), and a desorption temperature of 400°C. During the sorption cycle, the gas flows were maintained constant with the gas entering the top and leaving the bottom of the bed until uranium hexafluoride breakthrough was indicated by the detection unit in the trap outlet line. Concentrations in excess of 1 ppm. of uranium hexafluoride were considered breakthrough.

TABLE XIII

RESULTS OF 4-INCH DIAMETER SODIUM FLUORIDE TRAP SORPTION TESTS

Run Number	Total Flow, std.cfm.	Inlet Gas Concentration, %				Average Sorption Time, hr.	Desorption Time, hr.	Average Sorption Ratio, lb. UF_6/lb. NaF
		UF_6	F_2	ClF_3	N_2			
1	0.3	10	15	30	45	27.7	12	0.49
2 thru 14	0.3	10	15	30	45	6.3	12	0.28
15 thru 18	0.3	10	15	60	15	5.1	14	0.28
19 thru 23	0.3	10	15	0	75	8.3	14	0.47
24	0.3	10	15	30	45	5.0	14	0.25
A-1	0.3	10	15	30	45	8.2	14	0.45
A-2 thru A-6	0.3	10	15	30	45	5.2	14	0.26
A-7 thru A-10	0.3	10	15	0	75	3.9	14	0.21
B-1 thru B-6	0.3	10	15	30	45	2.9	14	0.10
B-7 thru B-15	0.3	10	15	0	75	3.0	14	0.11
C-1 thru C-5	0.3	10	0	0	90	3.9	14	0.13
D-1 thru D-5	0.3	10	15	0	75	12.1	14	0.67

On completion of the sorption cycle, the trap was purged, valved to reverse the gas flow through the bed, and heated to 400°C. A small flow of fluorine was used to sweep the desorbed uranium hexafluoride and to convert any uranium pentafluoride to uranium hexafluoride.

* Harshaw Chemical Company, Technical Grade No. Na-0101T-1/8.

As can be seen from the data, the sorptive capability of fresh pellets was approximately twice that of used material. The average capacity for used pellets in the first fifteen runs was about 0.28 pound of uranium hexafluoride per pound of sodium fluoride. Runs 15 through 18 show that increasing the chlorine trifluoride concentration from 30 to 60% had little effect on sorption. When the chlorine trifluoride flow was stopped in runs 19 through 23, the sorptive capacity almost doubled; resumption of the chlorine trifluoride flow in run 24 decreased the sorption to the earlier values. This phenomenon did not occur in the A and B series of test runs with different pellets. Run 25 was made to obtain breakthrough data for use in trap sizing and configuration. After the uranium hexafluoride detector showed a trace amount in the outlet gas, bulb samples were withdrawn periodically and were analyzed for uranium hexafluoride. Outlet uranium hexafluoride analyses were 0.3 mole percent 1 hour after breakthrough, 0.7 mole percent after 1-2/3 hours, and 5.5 mole percent after 2-1/2 hours. Data of this type should allow prediction of the performance of traps of various lengths.

The pellets were removed and inspected after run 25. The top 6 inches of the bed was found to be a powder, and the remainder of the bed was a mixture of powder and pellets. Inspection of individual pellets revealed that, while the pellets were quite hard, they were considerably smaller than when charged. In search of a material that would be more resistant to surface degradation, sodium fluoride pellets were heat treated for 5 hours at different temperatures. The properties of these pellets are summarized in table XIV.

TABLE XIV

EFFECT OF PREPARATION TEMPERATURE ON
SODIUM FLUORIDE PELLET CHARACTERISTICS

Treatment Temperature, °C.	Surface Area, sq.m./g.	Void Fraction	Stokes Hardness, div.*
540	2.149	0.406	1.0
590	0.118	0.120	5.5
650	0.061	0.104	6.5
700	0.031	0.038	8.0
760	0.060	0.097	8.0

* Comparative scale.

In the B and C series of tests, pellets were used that had been prepared by heating Harshaw sodium fluoride pellets to 650°C. for 5 hours. These pellets had a surface area of 0.110 sq.m./g. and a void fraction of 0.136. Temperatures and gas flows were similar to those in the original series of tests. It is apparent from the data that the sorptive capacity of

the 650°C. pellets was approximately one-half that of pellets treated at 540°C.

When the trap was emptied and the pellets were inspected, surface degradation was evident, although not so severe as with pellets treated at 540°C. There appeared to be some bonding between pellets; however, the clumps were easily broken apart, and no hard caking was observed. The small decrease in pellet degradation was probably more than offset by the loss in sorptive capacity.

A special sorbent pellet prepared at the Paducah Gaseous Diffusion Plant by pelletizing sodium bifluoride and furnacing at 760°C. was used in the D series of test runs. Gas flows and trap temperatures were again the same as those used previously. The data indicate that the sorptive capacity of this material is nearly three times that of the Harshaw type pellet used in all other runs; however, the fresh Paducah pellets sorbed less than used pellets which is contrary to experience with Harshaw pellets. When the trap contents were inspected on completion of the tests, severe pellet degradation was evident. The upper two-thirds of the trap was nearly 50% powder, and those pellets remaining were easily crumbled. Photographs of the two types of pellets before and after use are shown in figure 17.

After the Paducah pellet material was removed, the trap was filled with Harshaw sodium fluoride pellets which had been heat treated at 540°C. The bed was then subjected to temperature cycling in a nitrogen atmosphere to determine the effect of thermal shock on the pellet. An average cycle consisted of (a) maintaining a temperature of 120°C. for 2 hours, (b) heating to 400°C. in about 3 hours, (c) maintaining a temperature of 400°C. for 4 hours, and (d) cooling to 120°C. in approximately 1-1/2 hours. After seventeen cycles, the trap was opened, and the bed was inspected. No abnormal dusting was evident, and a Stokes pellet test showed no apparent change in hardness. Not surprisingly, these data and inspections of pellets used previously in the 4-inch trap support the belief that pellet degradation is chiefly, if not completely, a function of the amount of sodium fluoride-uranium hexafluoride complex made and decomposed each cycle.

The above pellets were then exposed to a flow of 0.3 std.cfm. of gas consisting of 10% uranium hexafluoride, 15% fluorine, and 75 % nitrogen at varying sorption temperatures. Under these conditions, the sorption ratios, pound of uranium hexafluoride per pound of sodium fluoride, at temperatures of 85, 120, and 175°C. averaged 0.32, 0.37, and 0.10, respectively.

It is apparent from the above tests that occasional changeout of trap charges will be necessary if sodium fluoride pellets are used for uranium hexafluoride sorption. The effective trap operating time will be influenced by the type of pellet used and the uranium hexafluoride loading. When there is no uranium hexafluoride sorption, as in the high temperature fission product removal trap, no pellet deterioration problems would be expected.

PHOTO NO. PH-65-716

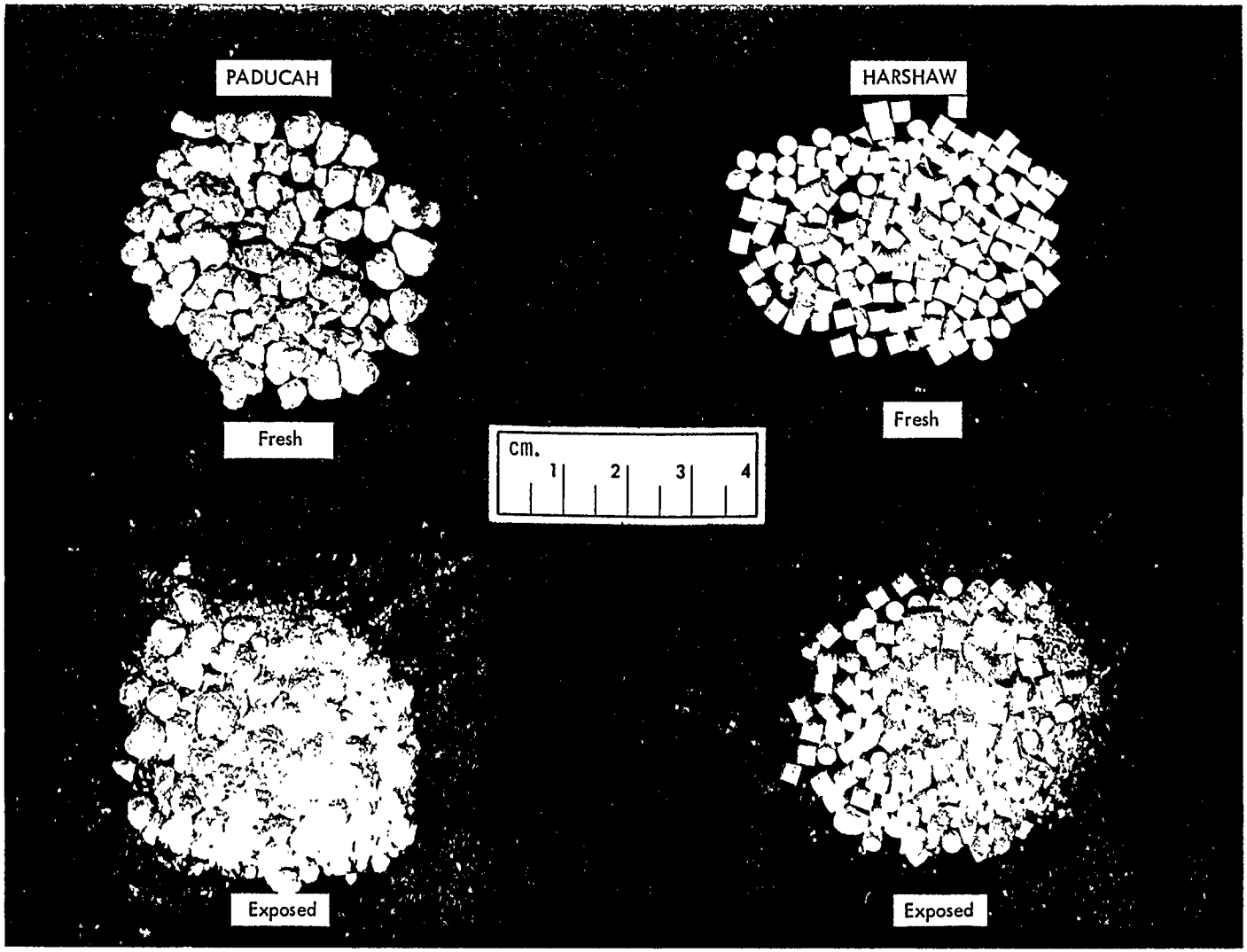

Figure 17
SODIUM FLUORIDE PELLETS

Trapping studies will be continued with different type pellets. Some tests are planned with pellets of mixed compositions.

Annular Pellet Trap

The primary problem encountered in designing large pellet traps for production use is one of heat transfer and resultant long desorption cycles. At this time, it is judged that large traps should be of annular design to minimize the distance from the center of the bed to the wall. A prototype unit consisting of concentric 5- and 12-inch diameter Monel pipes having a 60-inch bed height has been constructed. The annulus is baffled so that both the inlet and outlet pipes can be located at the top of the trap, and the bottom is coned to a central discharge port to facilitate removal of the pellets. The unit is heated electrically and is air cooled with the heating and cooling applied to the outside surface of the 12-inch pipe and to the inside surface of the 5-inch pipe. The trap and a flow diagram of the sorber loop are shown in figures 18 and 19.

The results of the annular trap sorption tests are shown in table XV. A total of 184.5 pounds of 540°C. treated sodium fluoride pellets was used as a charge for the first series of runs. In all runs, a sorption temperature of 120°C. and a desorption temperature of 400°C. were used. As was expected, the fresh pellets sorbed more uranium hexafluoride per pound of sodium fluoride than did the used pellets; however, the average sorption ratio amounted to only 0.17 pound of uranium hexafluoride per pound of sodium fluoride. Since this ratio was somewhat lower than expected, the pellets have been put in storage. At a later date, 4-inch trap tests will determine whether the low value is associated with pellet properties or with trap design.

To investigate the possibility of gas channeling in the upflow section, the annular trap was modified for the B series of runs to allow a separate parallel downflow of gases through each side of the annulus and a rejoined flow outlet at the bottom of the trap. Flows through each half were not measured and were dependent on the pressure drops through each of the pellet beds. The sorption ratios for a third charge of pellets were slightly lower than those obtained with the trap used as designed originally. Modifications to the trap and operating conditions are being formulated in an attempt to improve the performance capability.

Fluidized Bed

Pilot-plant studies are being made of a continuous system, figure 20, for the sorption of uranium hexafluoride from a process gas stream. Uranium hexafluoride diluted with nitrogen is first passed through sodium fluoride powder in a 6-inch diameter, 30-inch deep stirred fluid bed held at 120°C. Sodium fluoride is fed continuously, and the overflow powder is transported by the outlet gases to a filter mounted above the feed hopper for a ribbon flight screw desorber. The uranium hexafluoride-laden powder is fed from this hopper to the 6-inch diameter, 8-foot long screw, where it is heated to 400°C. to drive off the uranium hexafluoride. A small flow of fluorine is maintained through the screw to prevent formation of

DWG. NO. G-65-440

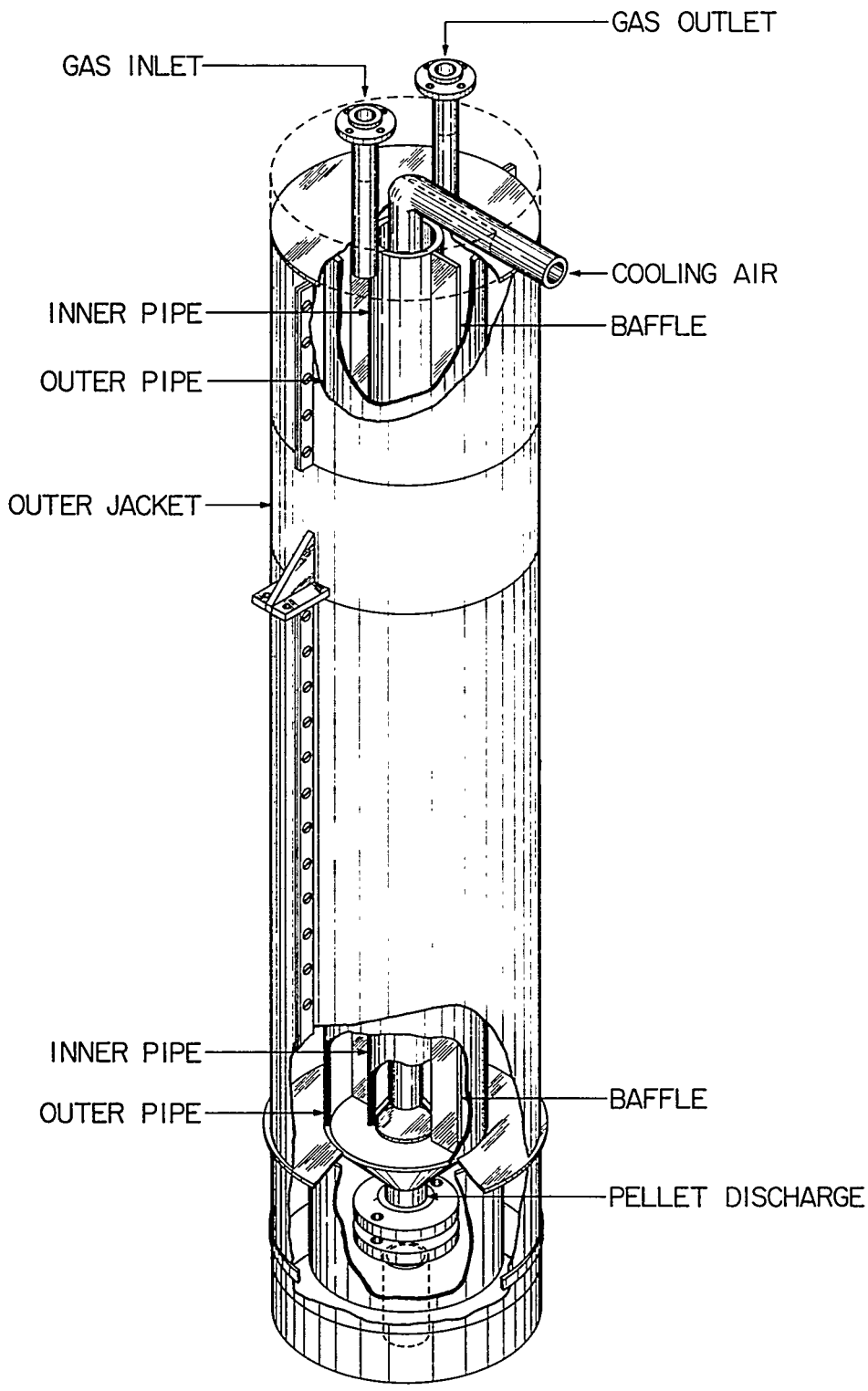

Figure 18
ANNULAR TRAP

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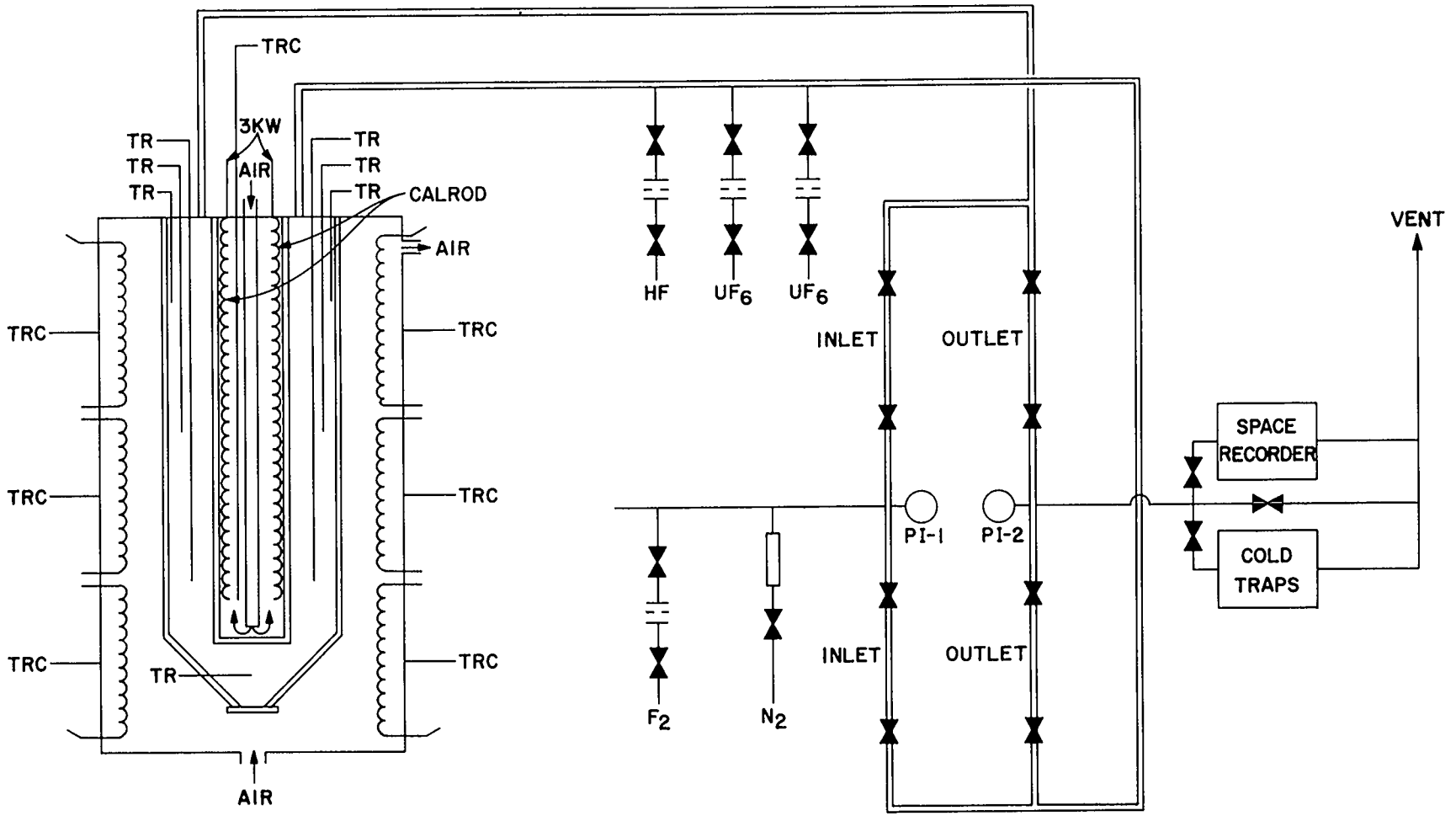

Figure 19

ANNULAR TRAP LOOP

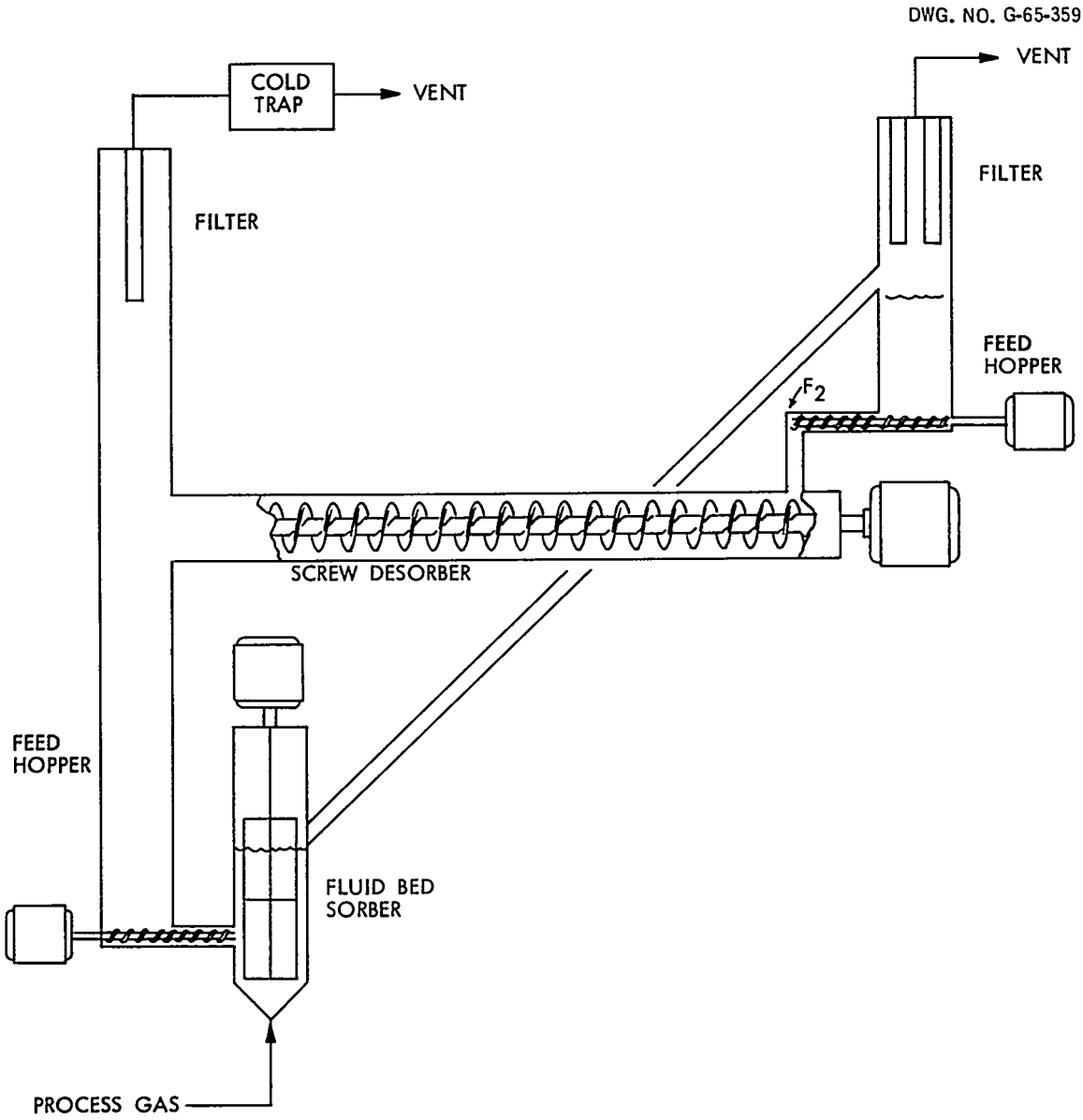

Figure 20

CONTINUOUS UF_6 SORPTION SYSTEM

uranium compounds other than the hexafluoride. The regenerated sodium fluoride falls into the fluid-bed hopper to complete the cycle. The total sodium fluoride inventory in the system is about 200 pounds.

TABLE XV

RESULTS OF ANNULAR TRAP SORPTION TESTS

Run Number	Total Gas Flow, std.cfm.	Inlet Gas Concentration, % UF_6	F_2	N_2	Sorption Time, hr.	Desorption Time, hr.	Sorption Ratio, lb. UF_6/lb. NaF
1	2.6	10	15	75	5.2	14	0.41
2	2.6	10	15	75	3.0	14	0.24
3	2.6	10	15	75	2.5	14	0.21
4	2.6	10	15	75	2.0	14	0.16
5	2.6	10	15	75	3.2	14	0.23
6	4.0	10	15	75	1.2	14	0.11
7	4.0	10	15	75	1.5	14	0.17
8	4.0	10	15	75	2.2	14	0.24
9	5.0	2	5	93	3.0	14	0.11
10	5.0	2	5	93	5.0	14	0.13
11	5.0	2	5	93	4.0	14	0.15
12	5.0	2	5	93	4.0		0.15*
B-1	2.6	10	15	75	3.7	14	0.32
B-2	2.6	10	15	75	2.1	14	0.18
B-3	2.6	10	15	75	2.2	14	0.15
B-4	2.6	10	15	75	2.0	14	0.12
B-5	2.6	10	15	75	2.0	14	0.16
B-6	2.6	10	15	75	1.8	14	0.15

* From flow measurements only. Not confirmed by cold trap weight on desorption.

Performance of the system has been very good for the range of conditions studied to date. The fluid bed has been operated with gas velocities of 0.15 to 0.70 foot per second, inlet gas uranium hexafluoride concentrations of 1 to 4%, and a bed temperature of 120°C. No problems have been noted with stirrer speeds as low as 20 rpm., and the average uranium hexafluoride concentration in the outlet gas has been consistently below 50 ppm. Essentially complete desorption of the uranium hexafluoride has been accomplished in the screw reactor at 400°C. with only a small flow

of buffering gas. Screw outlet gases containing as high as 40% uranium hexafluoride have been obtained. The rotational speed of the screw flight is 1 to 2 rpm.

The sodium fluoride used in the tests just described was prepared by heating sodium bifluoride cyrstals (100% through 20 mesh, 5% through 325 mesh) to 815°C. for 2 hours. The resulting crystals meet essentially the same particle size specifications as the starting material, have bulk and packed densities of 1.3 and 1.6 g./cc., respectively, and have a surface area of 0.2 to 0.3 sq.m./g. In the studies to date, only a small decrease in particle size to 10 to 15% through 325 mesh has been noted, and no effect on fluidization has been observed. If the powder is heated to only 535°C., however, rapid attrition occurs.

Continued operation of the pilot-plant system is planned. Studies will be made to determine the maximum capability of the unit and to investigate the effects of operating variables and of fission product accumulation. Since, for reprocessing use, the system must be essentially maintenance free, extended operation of the pilot plant at the expected conditions is necessary.

CONNECTORS

Since remote maintenance will be a requirement at many points in the proposed fuel reprocessing facilities, custom designed connectors must be used to facilitate removal of equipment. Service conditions for connectors at some points in the system will be quite rigorous because of the high temperatures and the corrosive gas atmospheres, particularly in view of the large size of some of the connectors, possibly up to 36 inches in diameter.

The first approach to the connector problem was to contact possible commercial suppliers. Several manufacturers of couplings were found who could deliver what appeared to be satisfactory products for electrical, instrument, and small process line use; however, only the Marman Conoseal clamp made by Aeroquip Corporation showed promise for application in the larger process lines. To broaden the possibilities for success, design work on adapting standard flat-faced flange closures for the required service was initiated. Results of the studies on the two types of connectors are described below. For both types, it was thought that double gaskets should be used so that the pressure between the seals could be monitored to detect leaks.

Marman Conoseal

A standard single gasket Marman Conoseal connector is shown in figure 21; a double seal unit is shown in figure 22. The initial problem faced in adapting the Marman connector for the intended service was selection of suitable materials for the flange and the gasket. Use of nickel for both parts was undesirable from the standpoint of galling. Duranickel which can be age hardened appeared to be the logical flange material based on corrosion data given in an earlier section of the report. Gaskets would

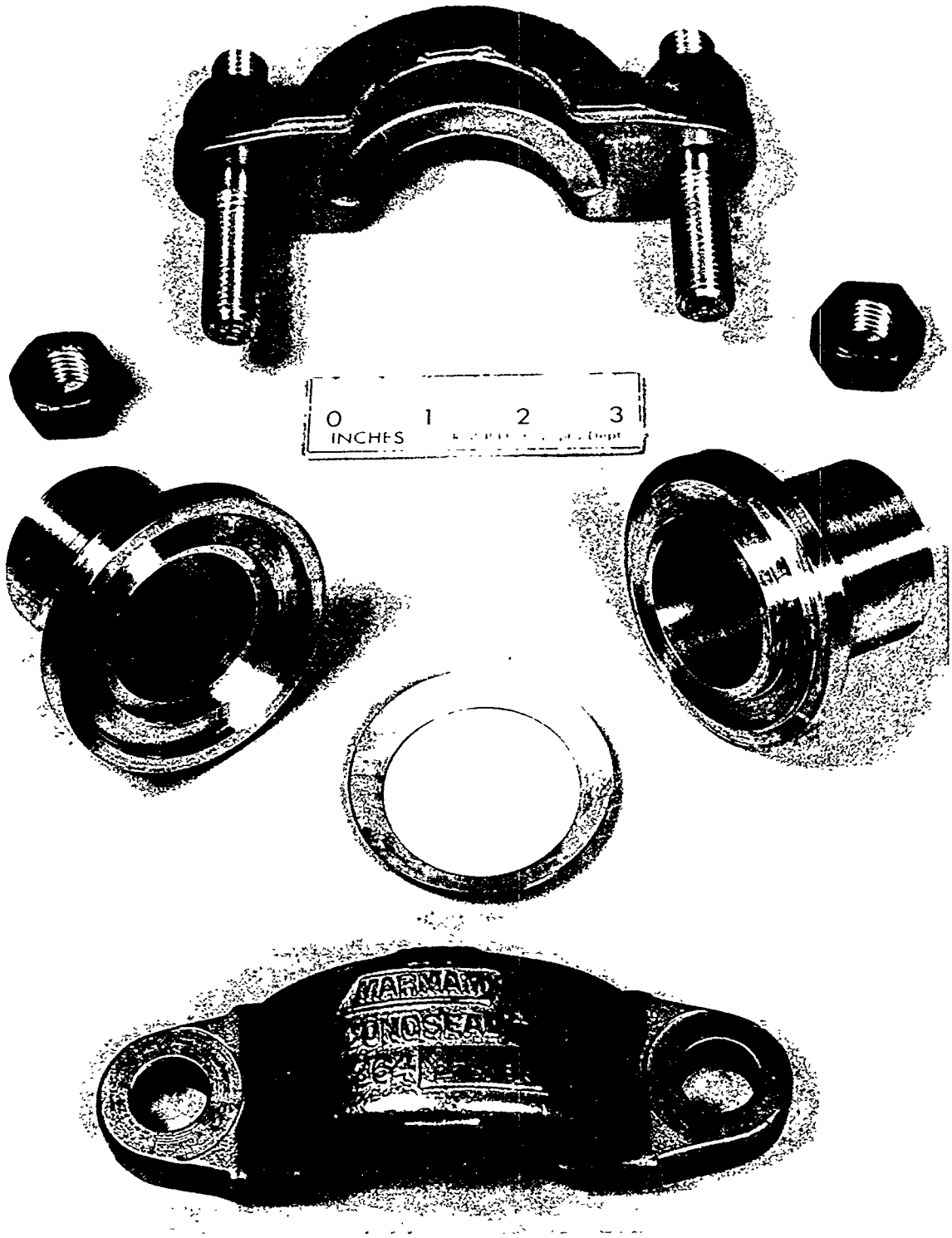

Figure 21
MARMAN CONOSEAL SINGLE SEAL

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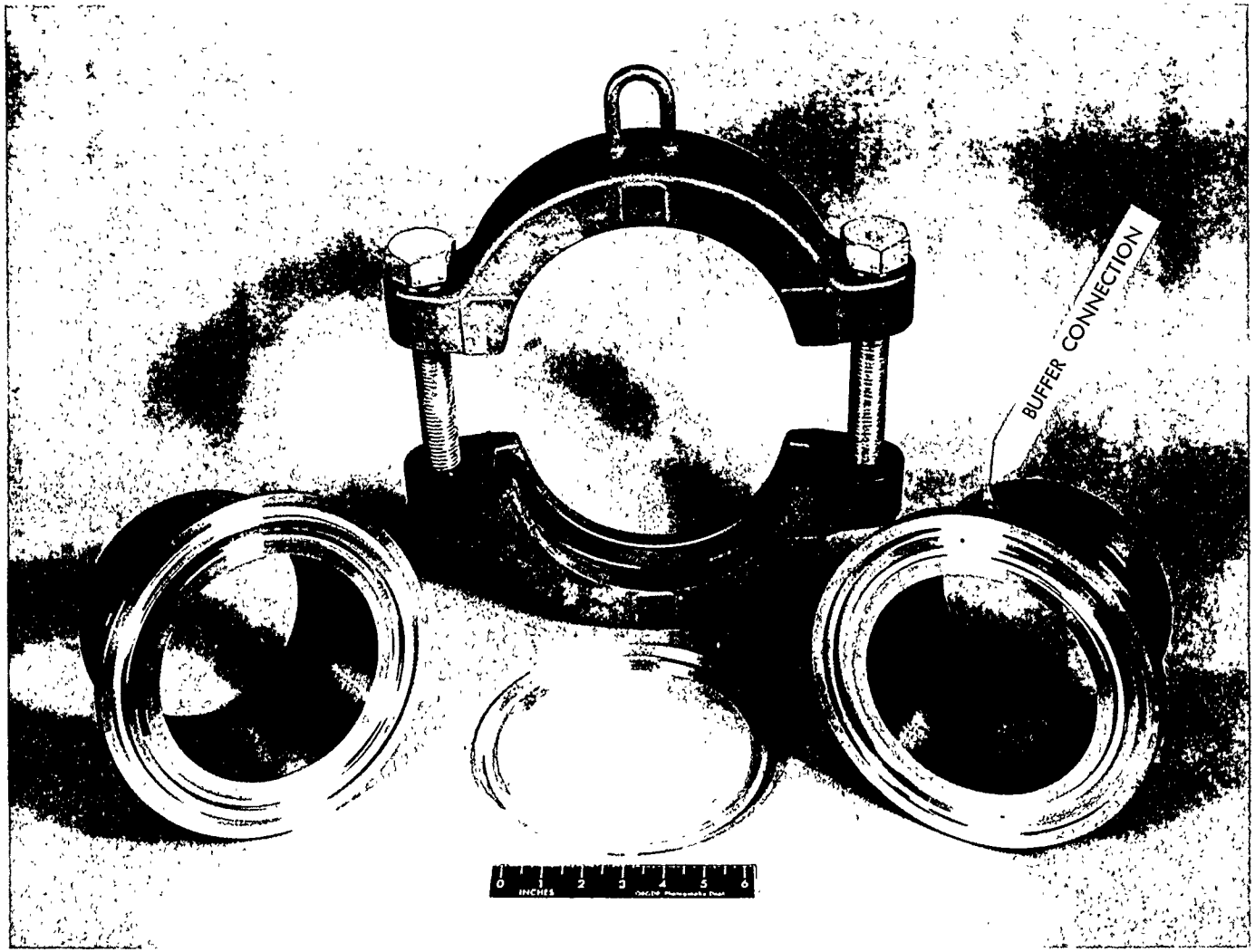


Figure 22

MARMAN CONOSEAL DOUBLE SEAL

then be made of the softer nickel. Another possibility was plating of a hard flange material with nickel, either by electroless or electrolytic means. Accordingly, 1-1/2-inch Marman couplings made of nickel, Duranickel, and stainless steel were ordered for testing. Larger units were not obtained because of the high price quoted for single custom-built units.

Good sealing was obtained with an electroless nickel-plated flange if a soft aluminum gasket was used. With a stainless steel gasket, however, spalling of the plate occurred. Electrolytic plating was not attempted because it was felt that deposition of an even coating on the contemplated flange face was improbable. The decision to omit the electrolytic plating possibility from the program was further strengthened by good results with the Duranickel flange.

A-nickel and Duranickel 1-1/2-inch Conoseal joints were checked for seating at room temperature using nickel gaskets. The as-received hardness of the components were Rockwell B-75, B-95, and B-54 for the A-nickel flanges, the Duranickel flanges, and the gasket, respectively. The Duranickel flanges were subsequently heat treated to a hardness of Rockwell C-40 before testing.

Both joints sealed effectively at a bolt torque loading of 20 foot-pounds. Each joint was opened and closed six times using the same gasket and resealed satisfactorily each time. It was somewhat difficult to join the two flanges with the provided clamps due to the bevel angle of the gasket. Considerable prying was also necessary to open the clamps to inspect the joint after each test.

The two Conoseals were then subjected to a heat cycling procedure. Both joints were torqued to a bolt loading of 30 foot-pounds, pressured internally to approximately 10 psig., and then placed in a muffle wherein the temperature was cycled between 95 and 540°C. and held at the maximum and minimum temperatures for 1 hour. After the sixth cycle, the A-nickel joint developed a leak and was subsequently retorqued to a bolt loading of 85 foot-pounds. Both connectors sealed for the remaining of the twenty-nine cycles of the test.

It was very difficult to open the joints at the conclusion of the experiment. The clamps on both assemblies required hammer force to separate them from the joint flanges. The A-nickel Conoseal appeared to have fused together at the gasket surfaces; however, the Duranickel flanges separated readily after the clamps were removed. Material hardness checks of the components gave a Rockwell B-58 for the A-nickel and Rockwell C-39 for the Duranickel flanges. This indicates that annealing of the A-nickel occurred, while the Duranickel hardness remained constant.

Results of the tests on their units have been discussed with Marman Conoseal representatives. It is their opinion that the clamp problem will probably be eliminated when the final design incorporates remote operator features and the use of dissimilar metals. The galling and fusing of the inner flanges and gaskets, resulting from the tests

described, figure 23, however, are not so readily explainable, and the Marman engineers are reviewing their design for possible modifications.

Flat-Faced Flange Connectors

Four typical flange arrangements were chosen for the test program. Basically, these units consist of two standard 150-pound, 4-inch flanges machined and drilled for buffer connections to accommodate the various style gaskets. The joint arrangements include (a) a double wire ring gasket made of 1/16-inch nickel wire, figure 24; (b) a serrated type nickel gasket, figure 25; (c) a multiple touchpoint style nickel gasket, figure 26; and (d) a flat nickel gasket with a double ring serration milled into the flange, figure 27.

Compression tests showed that nickel was an unsatisfactory flange material with nickel gaskets. Severe scoring of flanges was noted under pressures required to give good sealing. Scoring was even observed with soft copper gaskets which had been nickel plated.

Efforts were then concentrated on the use of Duranickel for the flat-faced flanges. The first flanges made of this material were welded to nickel stubs and were age hardened by the following procedure:

1. Heat to 595°C. in hydrogen atmospheres and maintain at that temperature for 16 hours.

2. Slow cool at 5°C. per hour to 480°C.

3. Cool at furnace cooling rate to room temperature.

Inspection of the flanges after hardening showed severe cracking, figure 28. At the recommendation of the International Nickel Company, the assembly was annealed by heating to 815°C. under hydrogen and then water-quenching before hardening. Use of this procedure has eliminated the cracking.

The flange assemblies described earlier have been fabricated from Duranickel, and testing is in progress.

COMPRESSORS

In the volatility flow sheets, recycle of process gas will be required in the fluorination steps and probably during hydrogen chloride decladding. The only commercially available pump application for these services is the diaphragm type unit. Accordingly, bids from various vendors of such units were requested, and a Corblin compressor was purchased through the American Instrument Company, Inc. The lack of choice of commercial compressors, coupled with the inherent low capacity of the diaphragm machines, made it desirable to consider utilization of ORGDP compressor development experience to fill the process needs. Accordingly, work was started at the ORGDP in designing a peripheral type compressor, a unit that has many potential advantages over the diaphragm type machine.

PHOTO NO. PH-64-475

Figure 23

NICKEL MARMAN CONOSEAL AFTER HEAT CYCLING

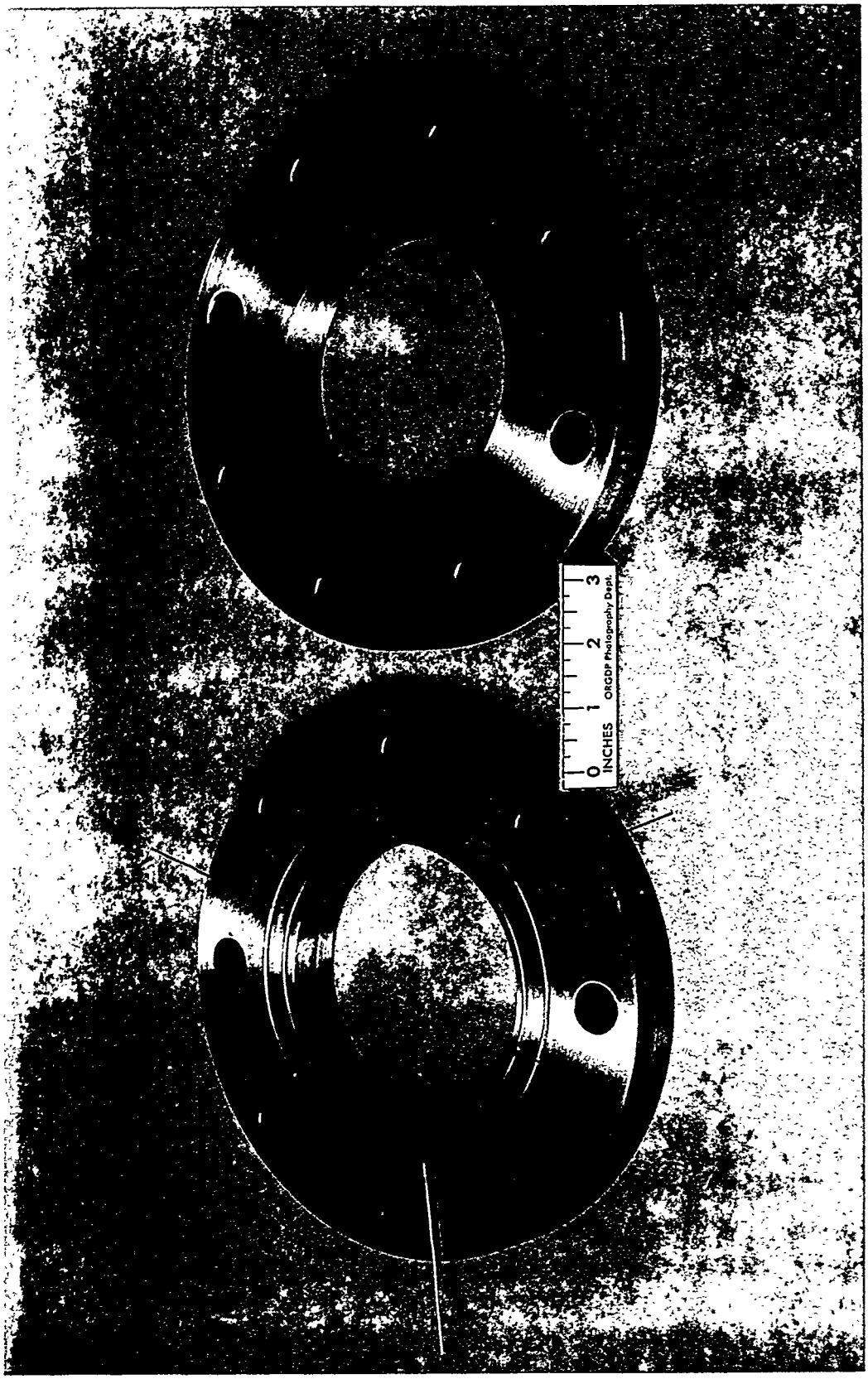


Figure 24
DOUBLE RING GASKET

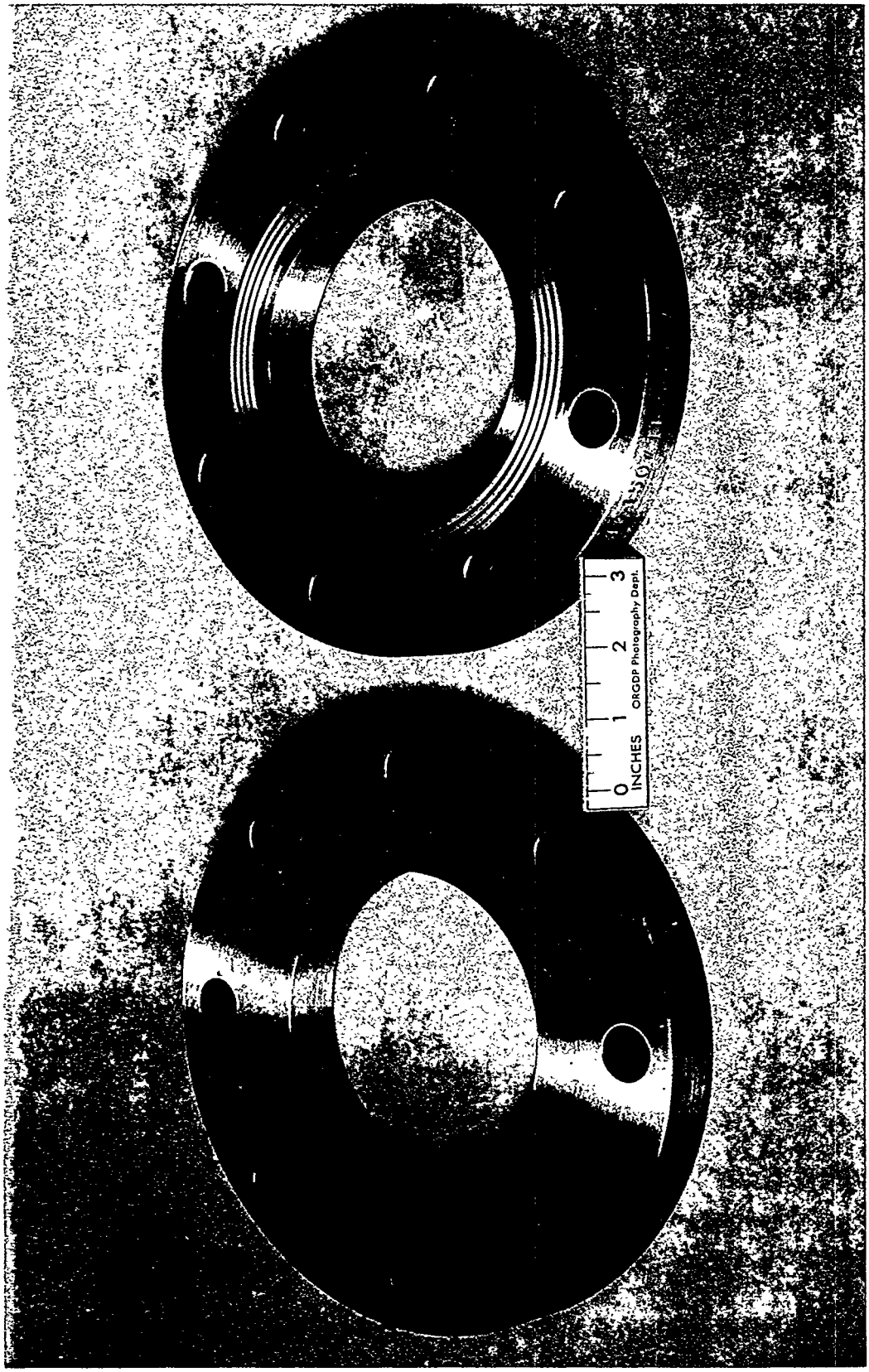
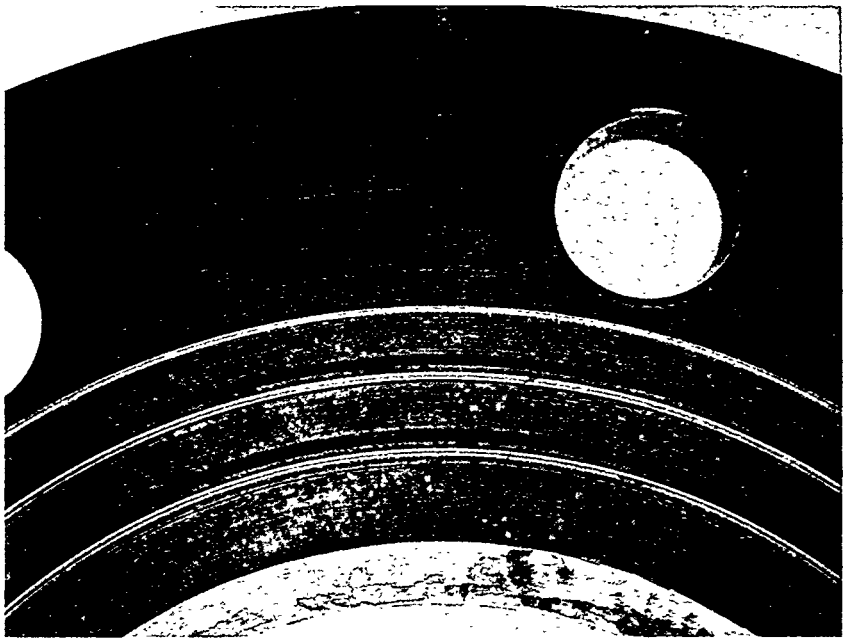


Figure 25
SERRATED GASKET

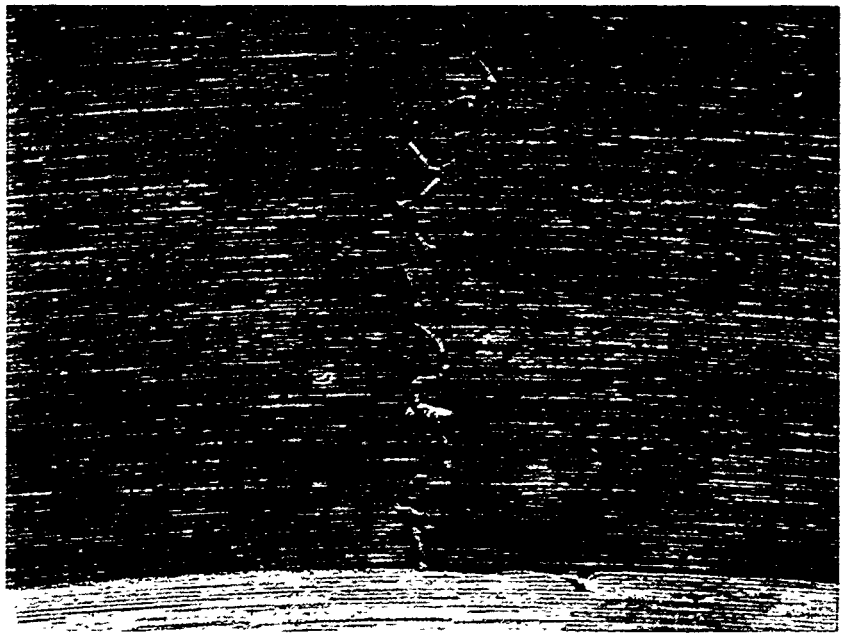
Figure 26
MILLED MULTIPLE TOUCHPOINT GASKET

Figure 27

MULTIPLE TOUCHPOINTS ON FLANGE - FLAT GASKET



Magnification 1X



Magnification 10X

Figure 28
DURANICKEL FRACTURES

Peripheral Compressor

Compressor requirements for a 1-tonne of uranium per day production line are summarized in table XVI. Studies at the ORGDP on the peripheral compressor indicated that it had attractive possibilities for meeting these requirements and would also operate reliably with satisfactorily low maintenance. A photograph of an experimental single-stage peripheral (sometimes called drag or regenerative) compressor is shown in figure 29. Positive displacement compressors, such as the reciprocating piston, the rotary lobe, and the diaphragm, are generally inferior because of problems associated with lubrication, wear, sealing, diaphragm life, and vibration. Compared with the centrifugal compressor, the peripheral type has simpler construction, operates stably throughout its flow range, and develops higher heads or pressure ratios for a given impeller speed and size.

TABLE XVI

DESIGN CRITERIA FOR
FLUID-BED VOLATILITY LOOP COMPRESSORS
1 Tonne of Uranium Per Day Line

	Compressor No. 1	Compressor No. 2
Suction Pressure, psia.	14.7	14.7
Pressure Ratio	2:1	2:1
Volume Flow, std.cfm.	50 to 150	25 to 50
Suction Temperature, °C.	-40 to +25	95
Process Gas Constituents	HCl, H_2, N_2	F_2, N_2, UF_6, ClF_3
Approximate Range of Molecular Weights	18 to 35	28 to 61
Maximum Inleakage, std.cfm.	0.2	0.2

In addition to selection of compressor type, it was necessary to choose the type of drive, bearing, and seal system. Two methods considered were (a) use of conventional bearings and motor with a shaft seal for protection from the process gas, and (b) use of process gas lubricated bearings with the motor operating in the process gas. Although the latter method has the advantage of a totally enclosed system with no inleakage, the technology, especially with regard to materials and motor protection, was considered insufficiently advanced to ensure a satisfactory compressor in the desired time.

The project therefore consisted of (a) development of the compressor aerodynamics; (b) development of a shaft seal design; and (c) combination of the aerodynamic, seal, shaft, bearing, and motor designs into a reliable, complete compressor. The goal was to evaluate the component and integrated designs and to construct a prototype compressor by July 1, 1965.

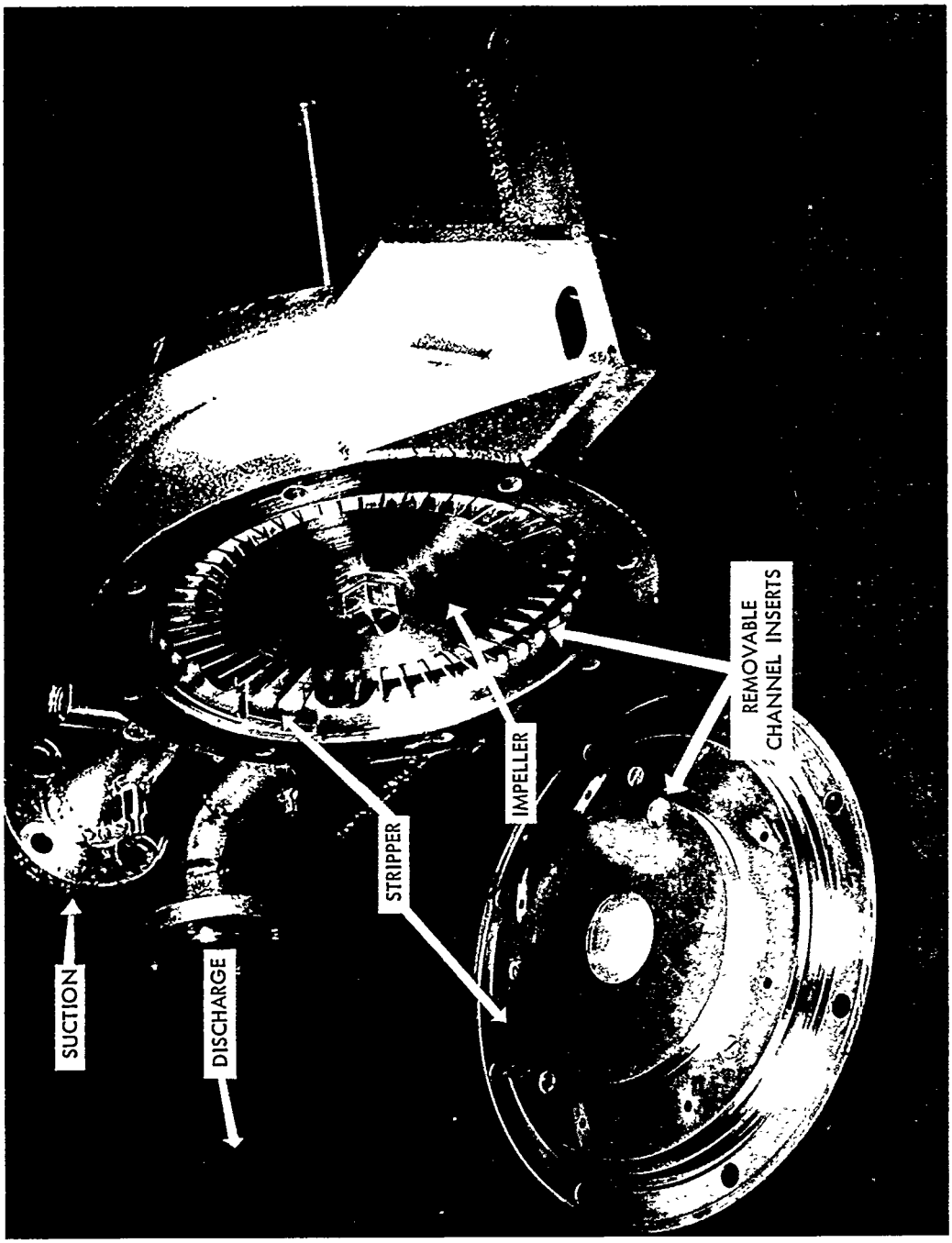


Figure 29
SINGLE STAGE PERIPHERAL COMPRESSOR

The component development and testing, the integrated design evaluation, and the design of a prototype compressor have been completed. Construction of the prototype is in progress and is scheduled for completion by June 30, 1965. The compressor, shown in figure 30, will have two stages on a single impeller, and an interstage cooler will be used to remove the heat of compression from the first stage. Through the use of removable inserts to change the channel dimensions, one basic compressor design will meet the requirements of both compressors operating at 11,000 rpm. The design consists of the impeller and motor rotor mounted on a single shaft supported in precision ball bearings. A nitrogen-buffered bushing seal will seal the process gas with a small amount of nitrogen inleakage. Motor and bearing cooling will be accomplished by a water jacket around the motor stator and an air thermal barrier between the compressor passages and the bearing housing. The expected compressor performance curves based on results of tests conducted in air are shown in figures 31 and 32. Descriptions of the work involved in arriving at the design of the compressor follow.

Seal Development. For the relatively high shaft speed necessary for these compressors, a positive clearance seal was considered more feasible than a contact seal. Three seal types studied in the program were (a) labyrinth, (b) screw, and (c) bushing. A stand for conducting the seal tests were constructed, and several designs of each type were evaluated using a 1.9375-inch diameter shaft size. Figure 33 is a photograph showing each seal type studied. All tests were made in air at speeds of 0, 8,600, or 11,000 rpm. Capacitance-type clearance probes were used at monitor shaft position during various operating conditions. Radial clearances of 0.002 inch and 0.003 inch were tested; other geometric variables included length of seal, eccentricity of hub to sleeve, number and shape of labyrinth teeth, and design of screw seal grooving.

Designs of all three seal types which would meet the inleakage requirements were tested, and the best was the bushing seal. Table XVII summarizes the performance of the bushing seal. The flows reported are actual cfm. at 1 psi. differential pressure. The effect of eccentricity was studied to predict the result of any misalignment upon assembly or operation. As may be seen in the table, even with a 3.2-mil radial clearance and a 0.5 eccentricity, a 2-inch long seal is adequate. The shorter length and larger clearance increase the freedom from assembly and operating difficulties. With precision ball bearings, a 3-mil radial clearance is considered quite practical. Also, the pressure differential of 1 psi. is considered adequate to prevent any back diffusion of the process gas outward through the seal past the buffer gas (nitrogen).

Compressor Aerodynamics. Part of the ORGDP peripheral compressor program included studies of channel and impeller geometries. Of the impellers tested, one with 0.500-inch deep blading was judged best. Stationary flow channel dimensions were systematically varied and tested with this impeller. Figure 34 summarizes the results obtained on nine channels which were closest to those required. Pressure ratio is plotted as a function of a dimensionless flow parameter which accounts for different fluid properties. Assuming two-stage operation, the approximate design points

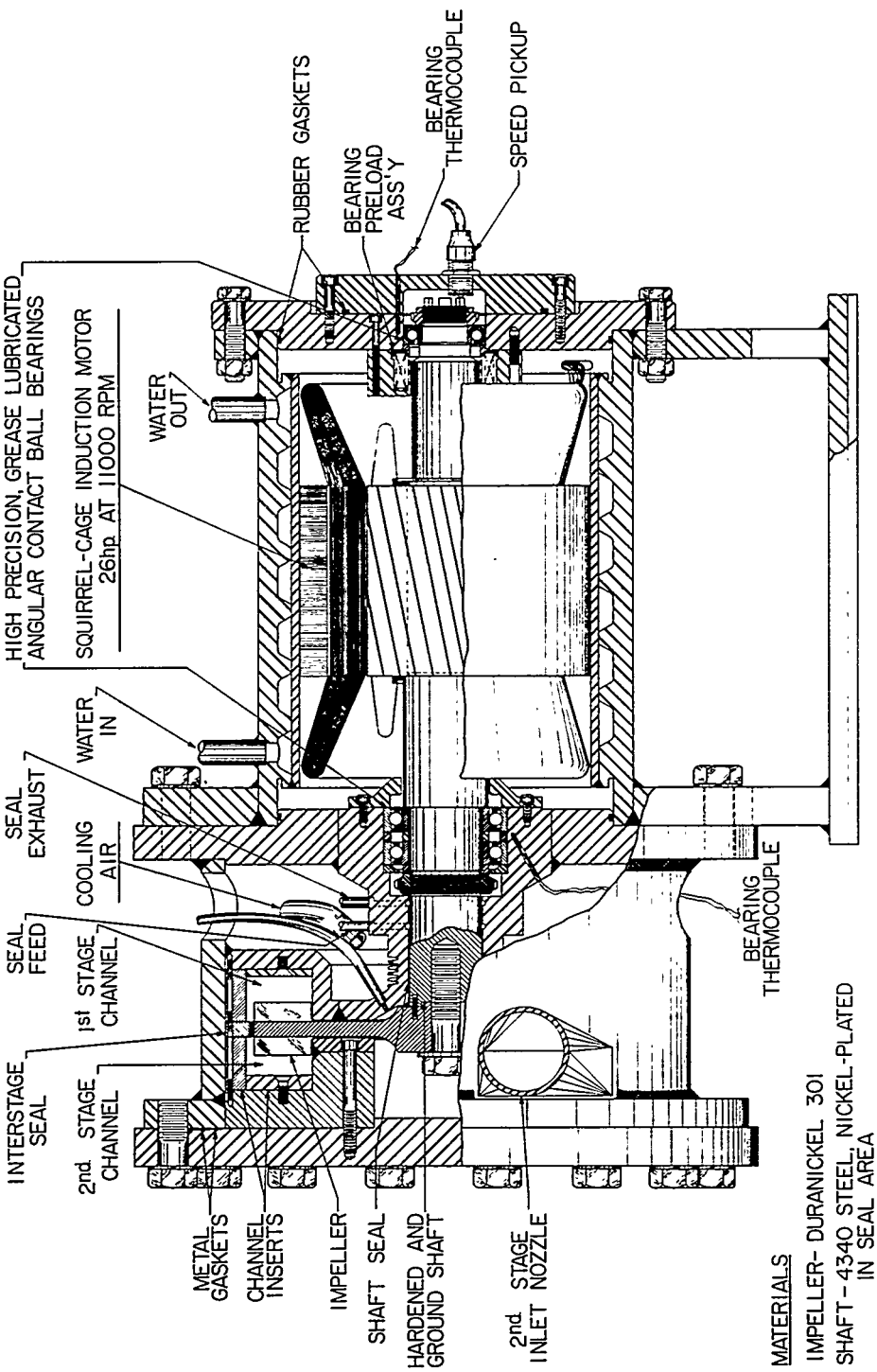


Figure 30

TWO-STAGE PERIPHERAL COMPRESSOR

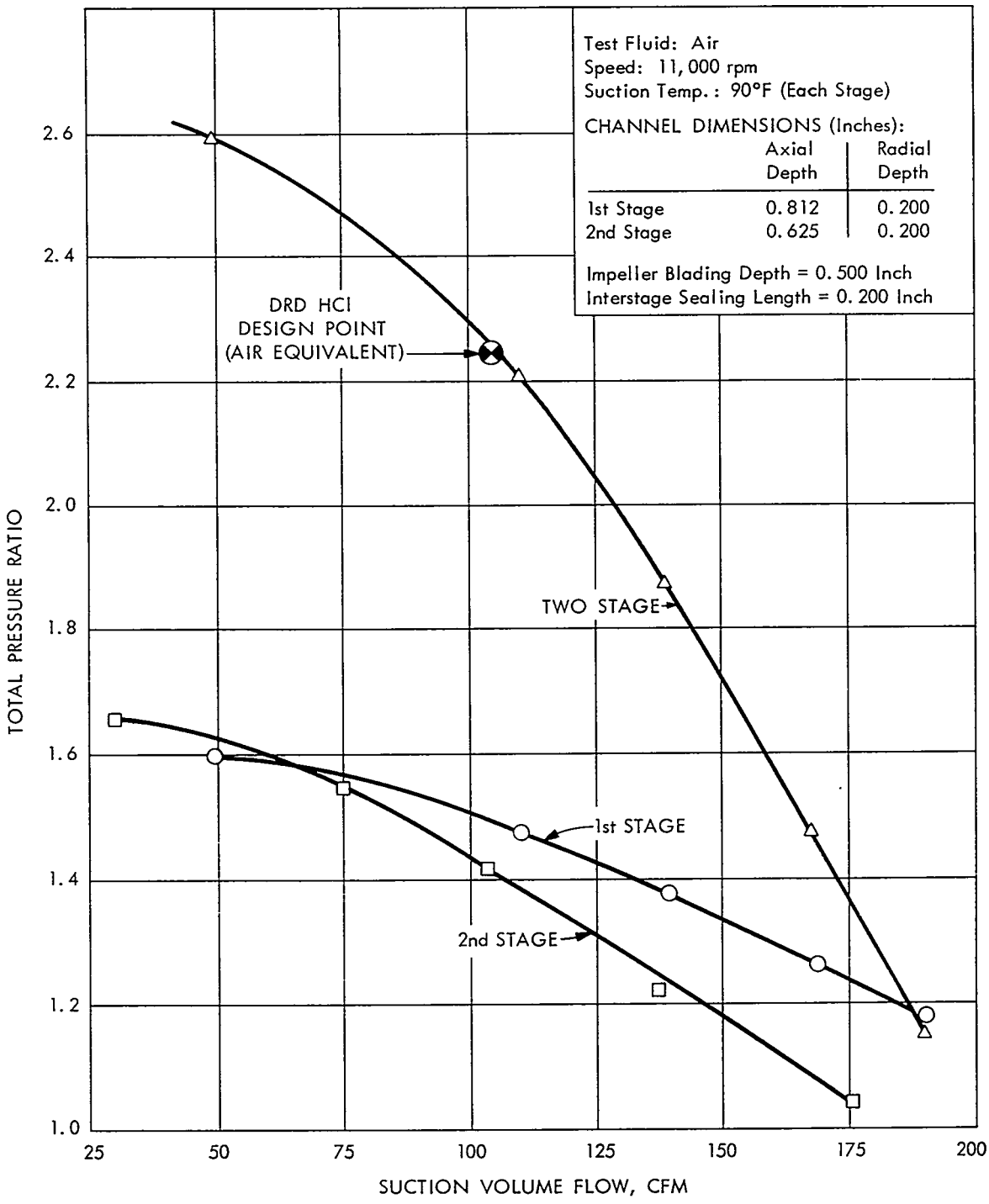


Figure 31
PERIPHERAL COMPRESSOR DUAL STAGE RESULTS

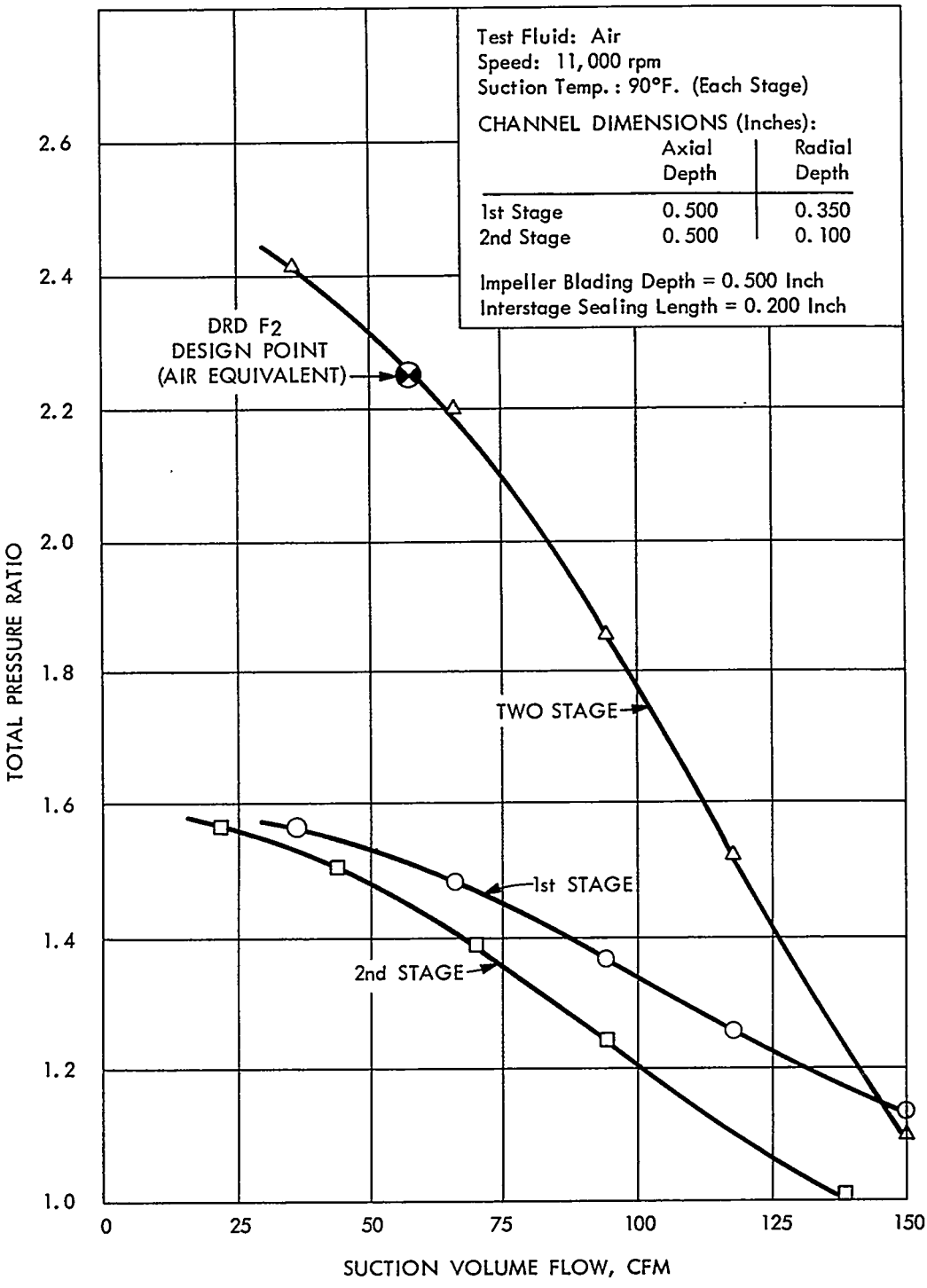


Figure 32

PERIPHERAL COMPRESSOR DUAL STAGE RESULTS

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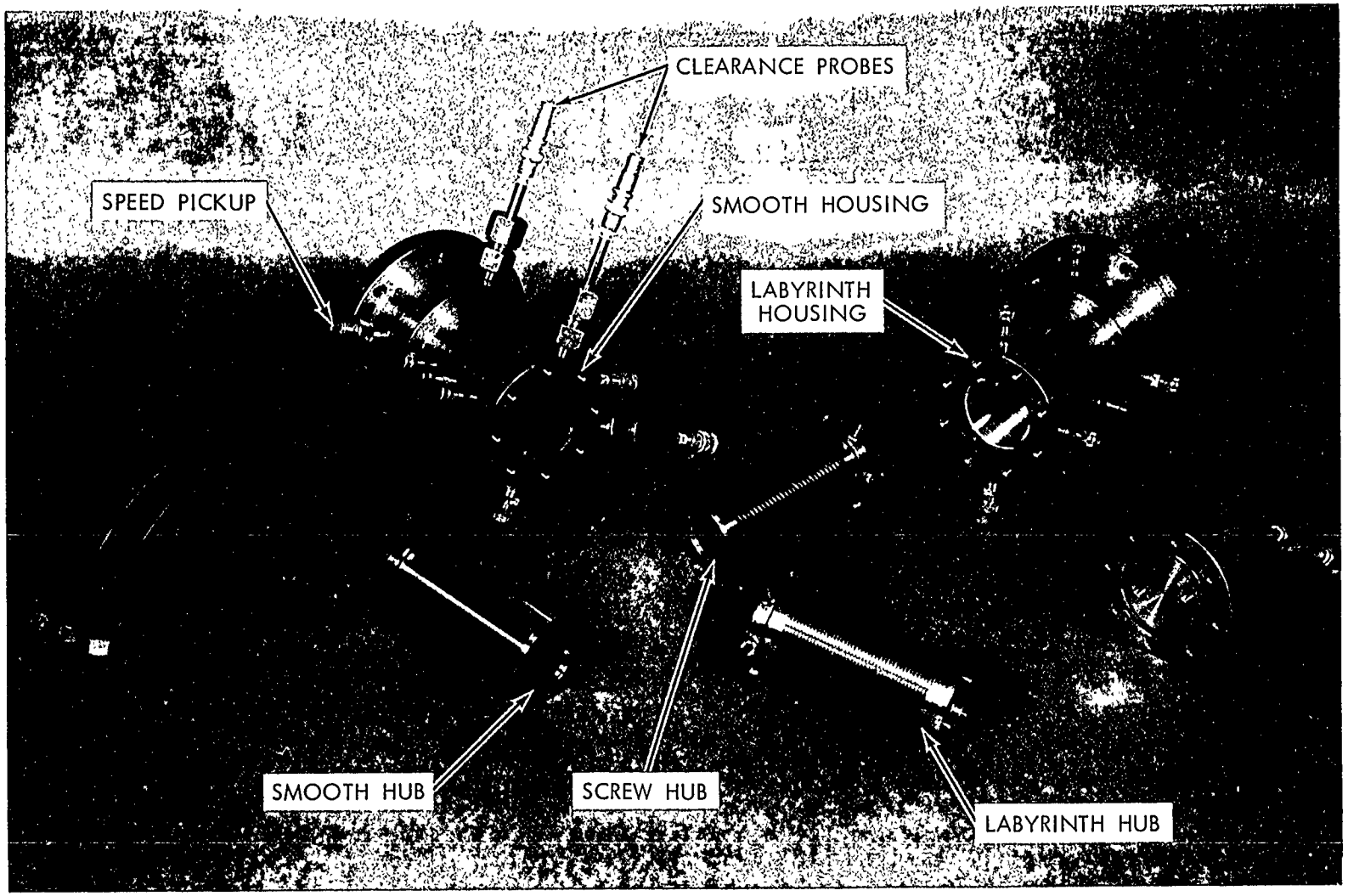


Figure 33
PERIPHERAL SEALS

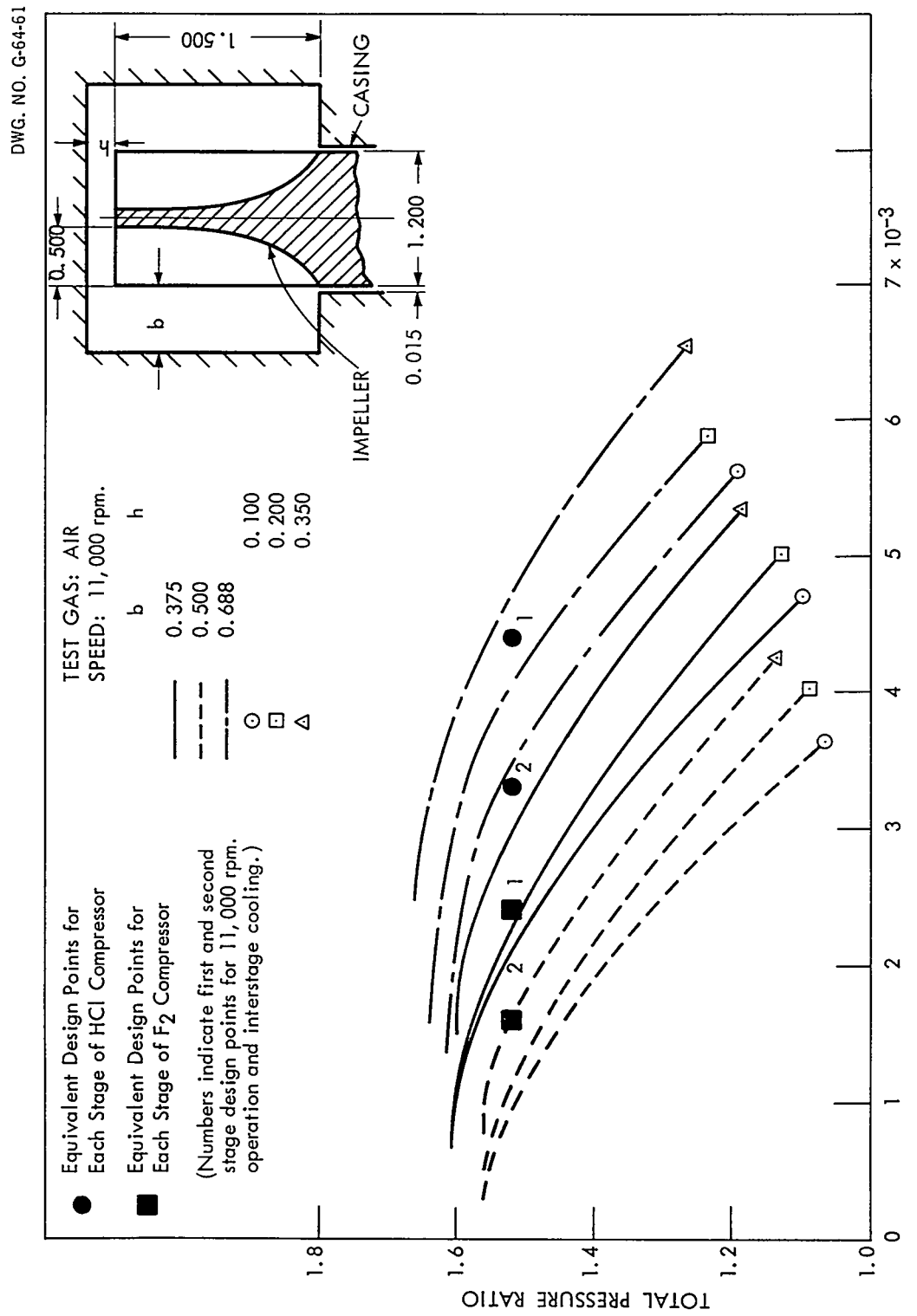


Figure 34

PERIPHERAL COMPRESSOR CHANNEL CHARACTERISTICS

for each stage of each compressor were included in the figure. These curves point out an important advantage of the peripheral compressor. With a basic impeller and housing design, the performance at a given speed can be varied greatly by the use of simple inserts to change the channel dimensions. These channel data were obtained with 0.015-inch impeller-to-casing clearance, which has proved to be satisfactory both aerodynamically and mechanically.

TABLE XVII

PERFORMANCE OF 1.9375-INCH DIAMETER BUSHING SEAL

Design	Leakage Flow, cfm. at 1 psi.	
	2 Inches Long	3-1/2 Inches Long
1. Required*	0.155	0.155
2. 0.0020-Inch Radial Clearance (Concentric)	0.018	0.010
3. 0.0032-Inch Radial Clearance		
a. Concentric	0.096	0.054
b. Eccentric (ϵ = 0.5)†	0.130	0.075

* Maximum permissible leakage based on 18 psia. average process pressure.

† ϵ is eccentricity ratio which is zero when hub is concentric with sleeve and unity when hub is touching sleeve.

It became apparent early in the program that two stages of compression would be necessary to permit reasonable operating speeds. Since the two sides of a peripheral impeller are independent of each other, mounting two stages on a single wheel with some interstage sealing device seemed feasible. This dual stage, single impeller concept would reduce the overhang moment on the shaft and would improve the rotor dynamic characteristics. The concept proved successful in performance tests and has been incorporated in the compressor designs. The data in figures 31 and 32 were obtained with a single impeller and a labyrinth seal to reduce cross-leakage between stages. This concept, along with a comparison of two impeller designs, is shown in figure 35. The new impeller design on the right is only 60% as heavy and has maximum stresses 59% as great as the conventional solid disc type impeller shown at left. The new type impeller is included in the prototype compressor design.

Test Rig Evaluation of Design Features. In addition to the development of the seal and compressor aerodynamic designs, it was considered important to study other design features of the compressor in an assembled configuration. These included rotor dynamic characteristics, bearing performance, motor and bearing cooling schemes, and motor performance.

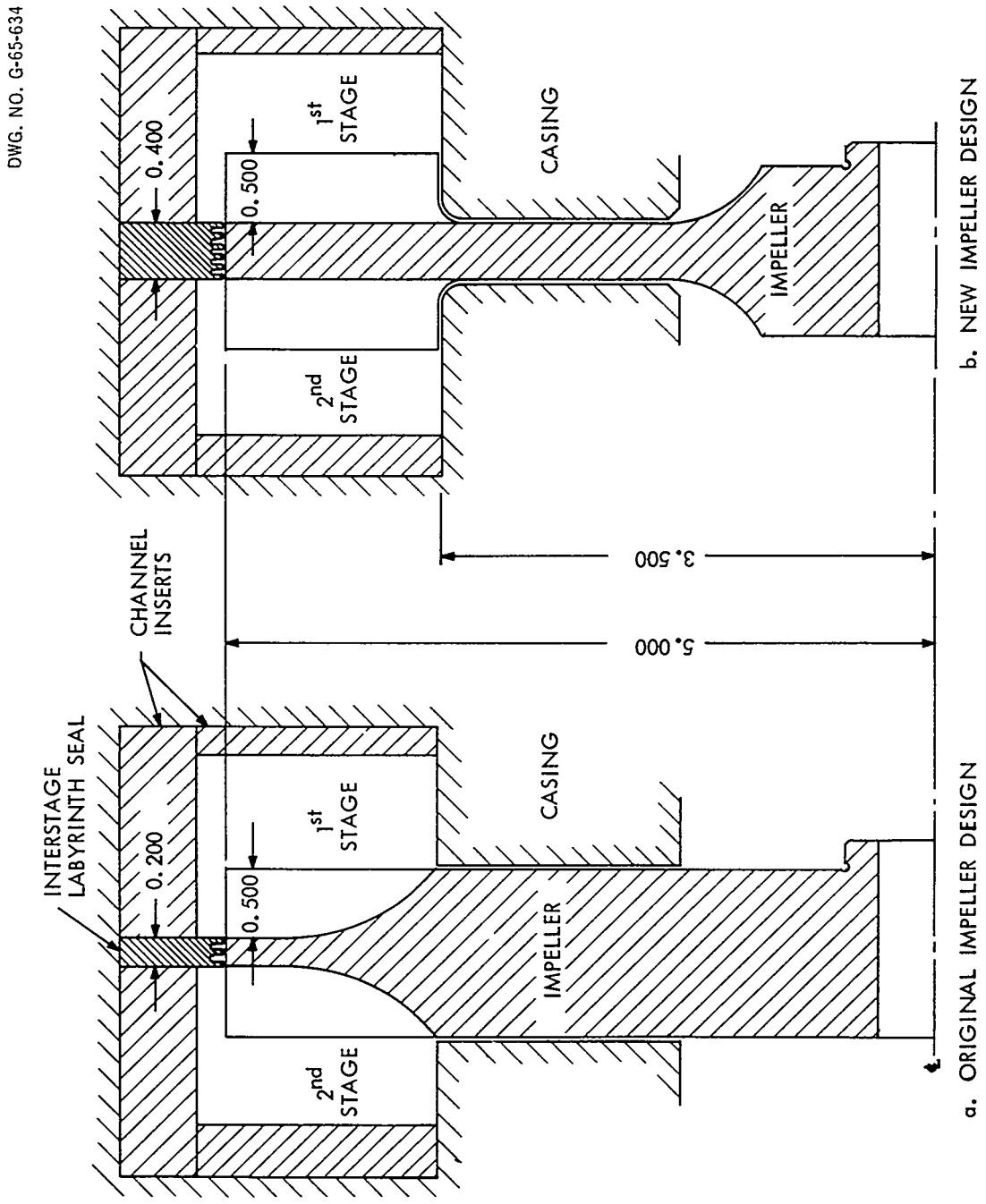


Figure 35
PERIPHERAL COMPRESSOR IMPELLERS

A test rig, built for other ORGDP programs, was ideally suited for this evaluation. The rig was instrumented with capacitance clearance probes to monitor rotor movement and with thermocouple and stick-on temperature indicators to determine thermal conditions under various modes of operation. The studies to date have verified the mechanical and thermal integrity of the compressor designs. Performance of the high precision angular contact ball bearings packed with Andok-260 grease has been good, and the motor and bearing cooling methods have proved satisfactory. Bearing temperatures less than 80°C. can be maintained at 11,000 rpm. under full load conditions (temperatures less than 95°C. are considered acceptable for these applications). Sizing of the motor, 26 hp., was adequate, and sufficient motor cooling is provided with a flow of 2 gallons of water per minute. By maintaining close but practical machining tolerances and by achieving a high quality of rotor balance, no difficulties with rotor performance were encountered. Testing is still in progress to confirm the aerodynamic performance of the new impeller design, figure 35, but preliminary data indicate the performance to be satisfactory. Actually, any discrepancies in either the compressor requirements or the correlation of performance from air to the particular process gas should be easily resolvable by adjustments in channel dimensions in the final installation.

Diaphragm Compressor

Performance specifications for the experimental diaphragm compressor are outlined in table XVIII. Multiple compressors would be needed for a production line capable of reprocessing 1 tonne of uranium per day, since there is no available commercial unit capable of satisfying flows and pressures shown in table XVI. The fluorine service application calls for a dual head assembly with a fluid media inert to fluorine, uranium hexafluoride, hydrogen fluoride, and chlorine trifluoride between the diaphragms. All parts exposed to the process gas are constructed of nickel. For hydrogen chloride service, a single diaphragm in contact with the process gas is sufficient. The diaphragms for the experimental machine are 26 inches in diameter.

TABLE XVIII

CORBLIN COMPRESSOR PERFORMANCE SPECIFICATION

Condition	Fluorine Service	HCl Service
Capacity, std. cfm.	12	20
Suction Pressure, psia.	14.7	14.7
Suction Temperature, °C.	95 Maximum	- 30 to + 25
Discharge Pressure, psia.	30	30
Gas to be Pumped	F_2, N_2, UF_6	HCl, H_2, N_2
Molecular Weight Range	28 to 61	18 to 35

The compressor was installed in a test loop as shown in the flow diagram, figure 36. A photograph of the unit is presented as figure 37. The system was arranged to test the remote head arrangement first, i.e., with the fluid volume between the diaphragms in the primary and remote heads filled with a fluorocarbon oil. As received from the vendor, no provision was made to compensate for fluorocarbon oil volume expansion and contraction resulting from temperature fluctuation; therefore, it was necessary to install pressure and vacuum relief valves for liquid volume control.

From the beginning, the pump exhibited an inherent vibration that required several revisions to the loop to provide flexible couplings on the pump and service headers. Calibrated reactance probes were installed at various positions on the primary and remote heads, and the vibration frequency and amplitude were measured on an oscilloscope. Four vibration pulses per pump revolution are detectable as shown in figure 38. Vibration movements as great as 0.100 inch on the remote head and 0.060 inch on the primary head were measured. Representatives of the pump vendor were informed of these results, and they stated that such vibration amplitudes were considered normal.

The maximum flow rate obtainable with the remote head was 10 to 15% lower than that obtained in the manufacturer's tests before shipment; therefore, transducers were installed at points in the fluorocarbon oil section to investigate the possibility of harmonic pressure pulse development in the length of pipe connecting the primary head to the remote head. Such a condition could affect the pumping performance of the unit. Evidence of some minor wave action was present; however, a maximum pressure pulse occurred simultaneously at all points in the oil system, figure 39. At this writing, it is concluded that the lower rate is probably caused by a small amount of air in the hydraulic fluid in the primary head.

The compressor loop is now being readied for a life test of the pump. It is planned to compress dilute fluorine at the maximum flow rate under suction and discharge pressures of 14.7 and 30 psia., respectively.

REACTOR FABRICATION PROCEDURES - WELDING STUDIES

The present specification concept for the primary fluid-bed reactor is that low carbon nickel will be used for surfaces in contact with the process. All welds on the equipment should be made using welding rod of the same material so that corrosion problems can be minimized. Considerable experimentation has shown the need for stringent preparation and welding procedures if acceptable welds of nickel-201 with nickel-201 rod that will meet the condition specified in pressure vessel codes are to be produced.

Many welding attempts were made in developing the recommended TIG weld. First, it was found that cleanliness of all components must be of the highest degree, since any nickel oxide present will cause welding difficulties and will create a porous weld. Flash pickling of all materials was found necessary. By dipping the work in a solution of 20% water-30% sulfuric acid-50% nitric acid containing 60 grams of sodium chloride per

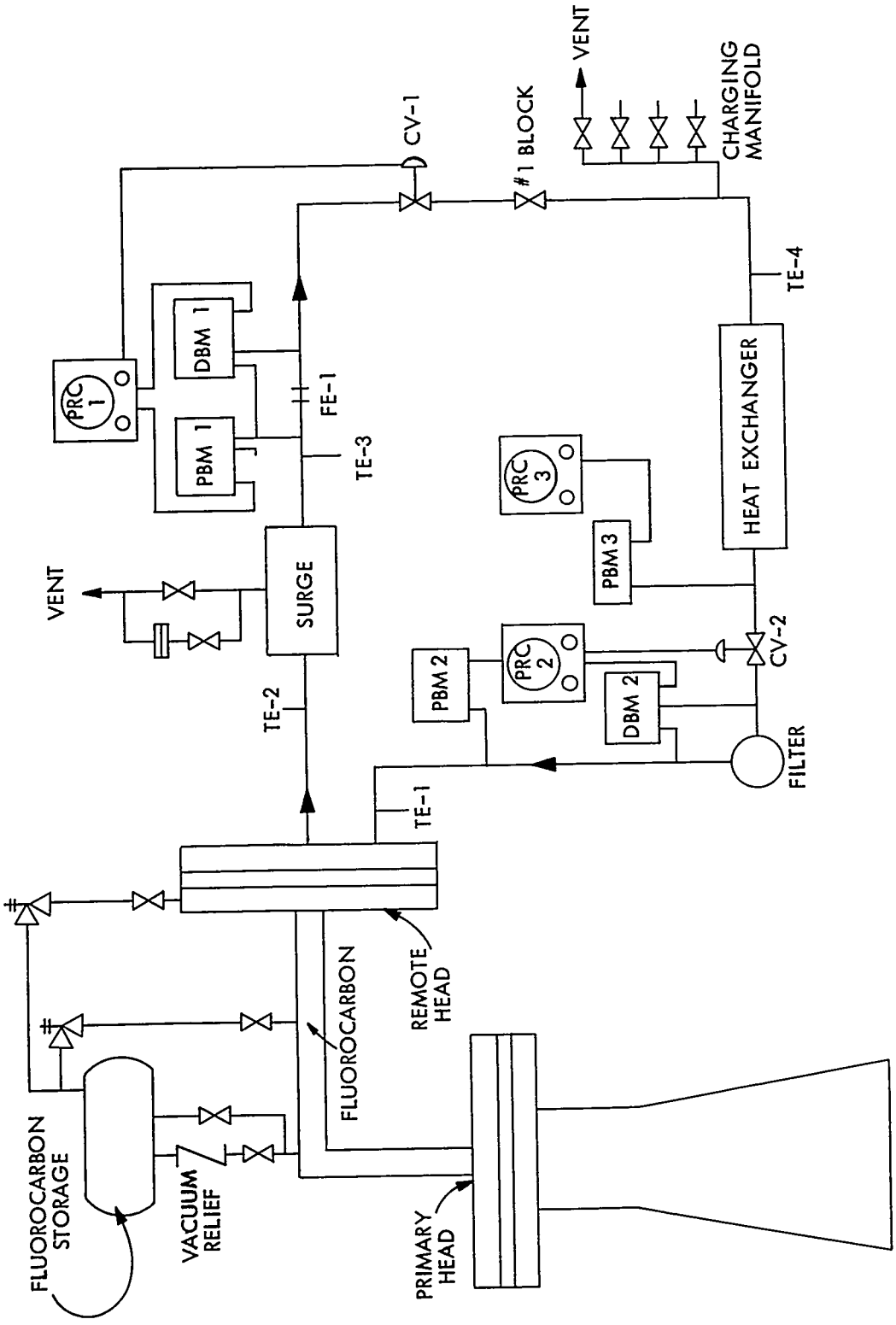


Figure 36

CORBLIN PUMP LOOP

PHOTO NO. PH-65-717

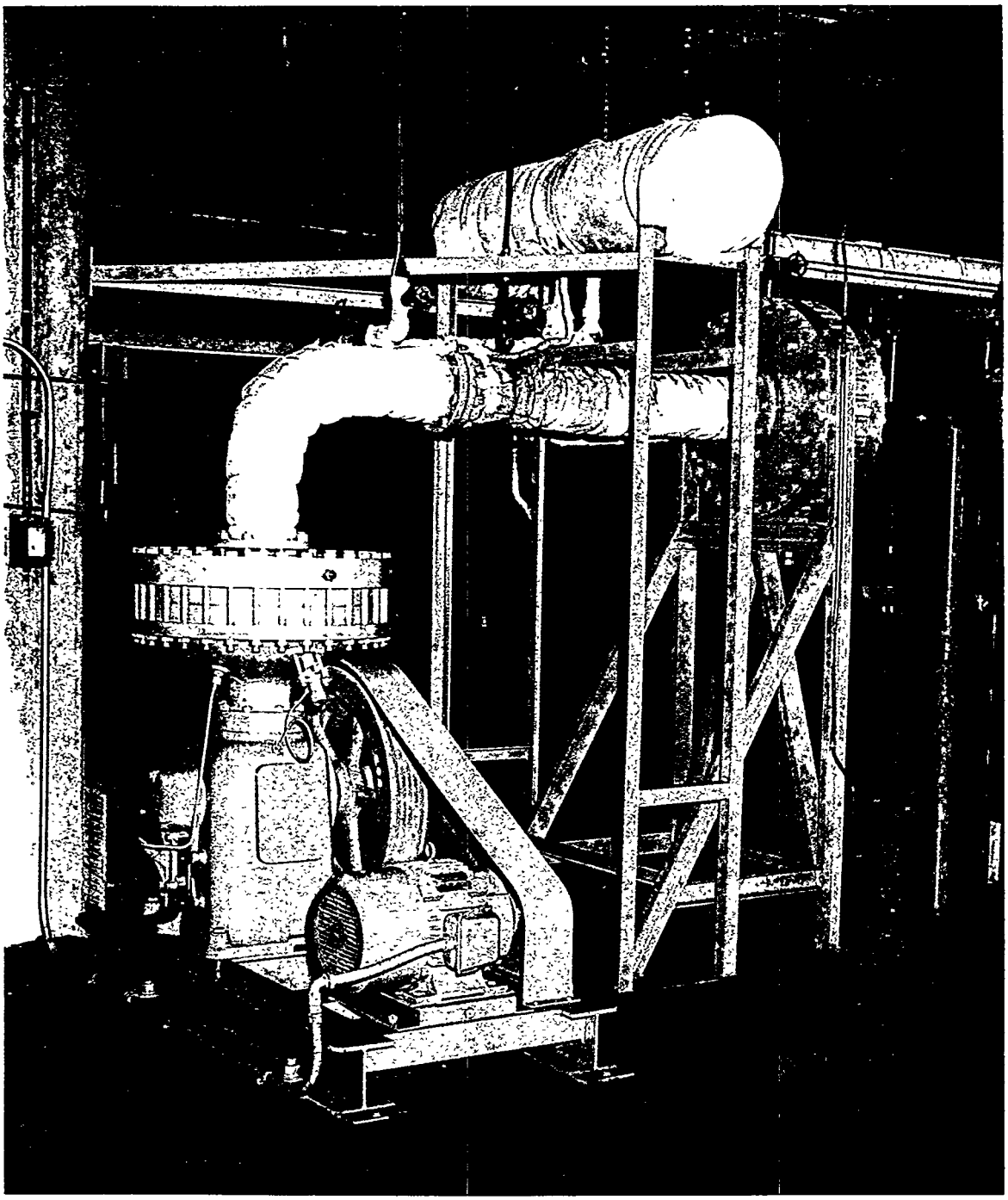
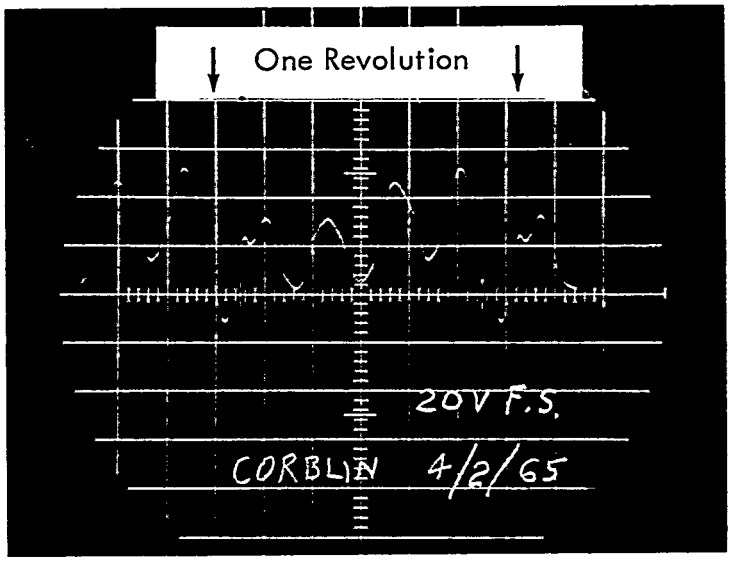


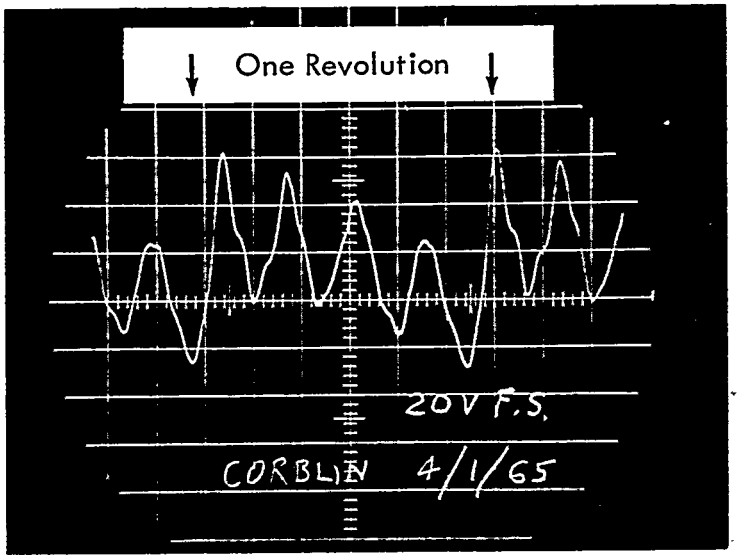
Figure 37
CORBLIN COMPRESSOR

Vibration Amplitude
19 mils per Division



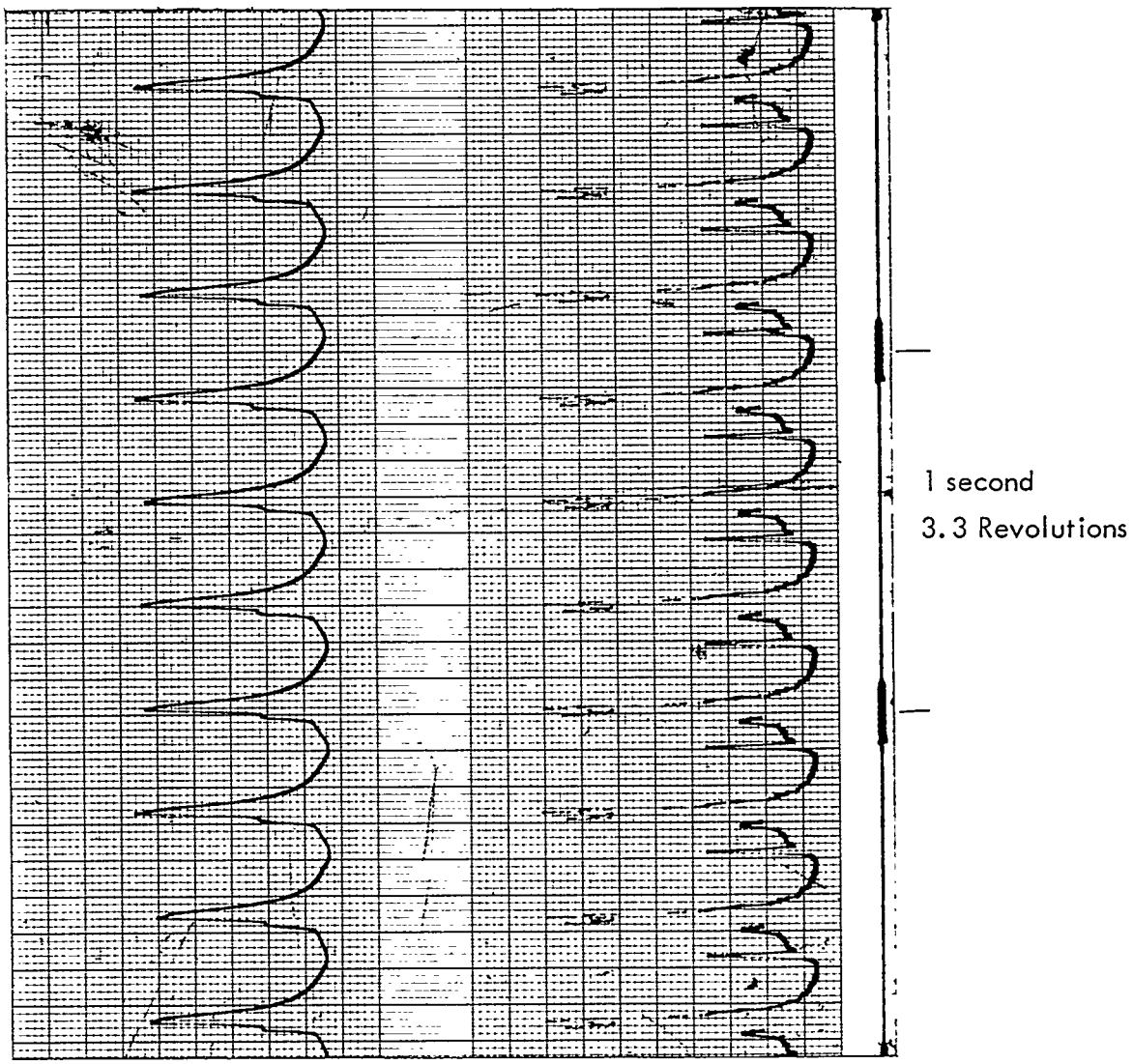
Primary Head

Vibration Amplitude
19 mils per Division



Remote Head

Figure 38
CORBLIN VIBRATION MEASUREMENTS



Pulse Calibration 2.5 psi. per mm.

Figure 39

CORBLIN FLUOROCARBON OIL PRESSURE MEASUREMENTS

liter and following this with a hot water dip, a bright, lustered surface was attained. Clean, white gloves were worn when handling the components.

Inasmuch as the filler rod is virtually unalloyed, melting and solidification occur abruptly without the incidence of a sluggish puddle. For this reason, the best welding control combination was found to be a high heat input with a fast travel rate. Arc amperages were varied between 50 and 120 amperes; arcs of 100 amperes for the root weld and increasing to 120 amperes for the face welds were necessary in butt welding 3-inch nickel pipe. The rod was fed into the puddle in fast, short jabs, but the tip was never removed from the inert gas shield of the torch, thus reducing the possibility of oxide formation.

A joint bevel angle of 75 degrees and a 1/8-inch gap were found to be the ideal conditions for a good weld. Both argon and helium torch and purge gases were employed in the tests with helium superior for both applications. A much higher back purge flow was required for the root pass to prevent oxidation and to provide adequate cooling.

Nickel-201 rods are not available commercially; therefore, nickel-201 sheet was slit, and the strips were swaged to provide a 3/32-inch diameter wire.

Successful welds have been made joining 3-inch nickel-201 pipe in the 2G and 5G welding positions. Face bend and root bend tests on these welds showed no cracking. Radiographs of the joint indicated no porosity or other defects. Tensile strength tests gave ultimate strengths of 55,000 to 60,000 psi. and elongations of about 20%. All of the above tests meet the ASME requirements for an acceptable weld; at the present, a formal welding procedure is being prepared for training and qualifying welders.

The future program will include studies of welding Duranickel to nickel-200 and to nickel-201.

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1968

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE GASEOUS DIFFUSION PLANT

operated for the ATOMIC ENERGY COMMISSION *under* U. S. GOVERNMENT Contract W-7405 eng 26

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OAK RIDGE GASEOUS DIFFUSION PLANT
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Digest of
Report K-1769

ORGDP FUEL REPROCESSING STUDIES SUMMARY PROGRESS REPORT JANUARY THROUGH JUNE, 1968

J. H. Pashley
R. B. Schappel

Process Systems Development Department
Gaseous Diffusion Development Division
Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
Nuclear Division
Oak Ridge, Tennessee

Report Date: January 13, 1969 Report Classification: Unclassified

The Oak Ridge Gaseous Diffusion Plant Gaseous Diffusion Development Division has participated in studies of a group of processes aimed at purifying and recovering valuable uranium and plutonium from spent nuclear reactor fuels. The program included two main phases: (a) preparation of conceptual plant studies with concomitant definition of problem areas associated with the process and technology and plant design; and (b) component development, including scale-up and testing of crucial process equipment and auxiliaries. The current report is the seventh and last in a series of progress reports issued semiannually. The topics covered include (1) the conceptual plant for the processing of spent, low enrichment LWR fuel; (2) scoping calculations for the volatility processing of spent Fast Breeder Reactor fuels in the areas of alumina usage economics, the increase in static bed with radioactive heat generation, the transfer of fission product heat from reactors, reagent requirements for plutonium fluorination, and nuclear safety; (3) process and reactor studies in the semiworks plant; (4) outlet gas filter studies; (5) uranium purification in a sorption-desorption system employing sodium fluoride; and (6) the testing of the ORGDP design peripheral compressor.

This report is 109 pages long and contains 33 figures and 21 tables.

Date of Issue: January 13, 1969

Report Number: K-1769

Subject Category: Chemical Separations Processes for Plutonium and Uranium

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J. H. Pashley
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NUCLEAR DIVISION
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

A B S T R A C T

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ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1968

This report is the seventh and last in the series of semiannual summaries of Oak Ridge Gaseous Diffusion Plant work in the United States Atomic Energy Commission-sponsored volatility process development effort. The work has been performed in conjunction with development programs at Argonne National Laboratory and Oak Ridge National Laboratory. The ORGDP program supported and extended the national laboratory efforts in two ways. First, conceptual plant studies leading to statement of technology problem areas, program analysis, and economic comparisons of alternative flow sheets were performed, and the cost of a 1-tonne of uranium per day processing plant was determined. Second, a component development program was conducted to cover scale-up and testing of crucial process equipment and auxiliaries. Emphasis was placed on the study of low-enrichment power reactor fuel reprocessing systems. The possible applications of volatility techniques to fast reactor fuels were also considered, and some scoping studies in this area were conducted.

The program at the ORGDP was phased out as of July 1, 1968, in accordance with the AEC decision to discontinue studies on the application of volatility techniques to the processing of low enrichment power reactor fuels. Aqueous methods have been demonstrated to be successful and sufficiently economic to support this segment of the nuclear power industry; nevertheless, the dry processing route appears to be potentially competitive economically with the aqueous methods. Unfortunately, the advantages cannot be firmly established because development work is incomplete.

SUMMARY

ENGINEERING STUDIES

Topical reports were prepared for publication on the conceptual volatility processing plant, the design of cold traps, and plant nuclear safety studies. In addition, scoping calculations were made for volatility applications in Fast Breeder Reactor fuels reprocessing.

CONCEPTUAL PLANT STUDIES

The report on the 1-tonne of uranium per day conceptual plant is complete and will be published soon. Included in the report are sections on bases for the study, process technology, process description, process critique, general facilities, safety, plant staff, costs, and conclusions and recommendations. The capital cost of the plant is estimated at 33 million dollars when a 25% contingency is included. The total unit fuel reprocessing cost (capital charge plus operating cost) is $27.32/kg of uranium.

FBR CALCULATIONS

Scoping type calculations for FBR fuels were made to provide input information for ANL volatility applications studies. The FBR fuel charges were assumed to be 50% core material (20% plutonium dioxide and 80% uranium dioxide) and 50% axial blanket material, while the core burnup and the specific power were 100,000 Mwd/tonne and 200 Mw/tonne, respectively. Calculations were made in the areas of alumina usage economics, the increase in static bed with radioactive heat generation, the transfer of fission product heat from reactors, reagent requirements for plutonium fluorination, and nuclear safety.

Alumina Usage Economics

Utilization costs, i.e., the total of alumina costs at $0.19/lb, plutonium loss penalty at $10/g, and waste storage investment, were computed for alumina usages of from 0.25 to 5.0 kg of alumina used per kilogram of uranium plus plutonium processed and for 30- and 120-day cooled fuel. The results indicate that a reduction in the amount of alumina used is desirable, as might be expected, and that some storage cost savings may be obtained by processing longer cooled fuel; however, the savings do not appear to be great.

Static Bed Temperature Increases Due to Radioactive Heat Generation

Estimates were made of the centerline temperature rise rates which might be encountered in various size solid cylindrical and annular beds containing FBR fuels if fluidization were lost during processing. Fuel cooling times of 30 and 180 days were considered. Calculations were made for the conservative case where fluidization is lost immediately after removing all the plutonium and uranium from the bed, with only the alumina and fission products left behind. The ratio of alumina to fuel prior to fluorination was assumed to be unity initially. The bed density, heat capacity, and thermal conductivity were taken to be 135 lb/cu ft, 0.26 Btu/lb-°F, and 0.26 Btu/hr-ft-°F, respectively.

The computed temperature changes are plotted versus time after loss of fluidization for cylindrical beds with radii of 0.5, 1.0, and 1.5 feet. The same type plots have been prepared for annular beds where the central diameters are 4, 8, and 12 inches, and the annulus dimensions are 3, 4, 6, and 8 inches. With such data, estimates can be made of permissible downtime limits before effective corrective action need be taken to avoid sintering.

Transfer of Fission Product Heat From Fluid-Bed Reactors

Computations indicate that fission product heat releases as high as 30,000 Btu/hr-cu ft of reactor bed are possible when FBR fuels are processed in fluid beds at low alumina usage ratios. The heat fluxes

required to remove this amount of heat was found to be no greater than 15,000 Btu/hr-sq ft of wall area for fluid-bed reactors up to 24 inches in diameter. Since fluid-bed heat fluxes in the range of 10,000 to 15,000 Btu/hr-sq ft can be achieved with a properly designed cooling system, reactor diameters up to 24 inches seem practical from the heat transfer standpoint.

Plutonium Fluorination Requirements

The production capabilities of 5- to 25-inch-diameter reactors were calculated for continuous fluid-bed fluorination of the plutonium from FBR fuels at bed temperatures from 300 to 500°C. Interest was focused, in particular, on the time requirement and the reaction rate for the step. A gas velocity of 1.0 ft/sec and a pressure of 1 atmosphere of fluorine were assumed. In addition, the product gases were assumed to contain equilibrium proportions of plutonium hexafluoride and fluorine at reaction bed temperatures.

Calculations were also made for overall fluorine requirements in batch fluorination with various plutonium charges and fluorine flow rates. The bed temperature was assumed to be 300°C initially and to rise to 400°C over the course of the reaction at a rate of 20°C/hr. During the latter stages of the reaction when the plutonium concentration in the fluid bed becomes small, the plutonium hexafluoride-to-fluorine ratio in the off-gas will likely become smaller than the equilibrium value because increased quantities of fluorine will be necessary to complete the step.

The results of the continuous and the batch process calculations are presented in graphical form. Each graph is arranged so that the average fluorination rate can be obtained as a function of the operating parameters within the ranges selected for the study.

Nuclear Safety

Studies were made of the nuclear reactivities of plutonium dioxide and plutonium tetrafluoride, at various densities, in spherical, infinite annular, infinite and finite slab, and infinite and finite cylindrical geometries.

The critical radii for spheres and infinite cylinders containing homogeneous mixtures of plutonium dioxide and alumina and also plutonium tetrafluoride in alumina were estimated by use of the ANISN Neutron Transport Code. The radii for spheres and infinite cylinders were found to be smaller for high density (9 g/cc) plutonium dioxide cases than for the fully dense (7 g/cc) plutonium tetrafluoride cases.

The critical inner radii were computed for vessels with 3, 4, 6, and 8-inch annular thicknesses containing homogeneous mixtures of plutonium dioxide and alumina. The effective neutron multiplication factor first increases as the radius of the inner cylinder is enlarged at constant annular thickness. The k_{eff} then reaches a maximum and eventually decreases and approaches the value for an infinite slab.

The Monte Carlo code was used to calculate the reactivities of finite cylinders and slabs of plutonium tetrafluoride. Bare vessels, as well as vessels with top and bottom reflection and nickel cladding, were considered. Reflected 10-inch-diameter cylinders containing plutonium tetrafluoride at 3 g/cc and 4-inch-thick by 2-foot-long slabs of plutonium tetrafluoride with compound densities of 3 and 5 g/cc were computed to be subcritical regardless of height.

PROTOTYPE TESTING AND EVALUATION

The projects during the final report period included runs in the semiworks facility, filter multiple exposure tests, product purification by sorption on sodium fluoride, and operation of the peripheral compressor. A movie showing results of bromine pentafluoride spill tests has been prepared.

PROCESS AND REACTOR STUDIES

The semiworks reactor system program was concluded with further elutriation tests and studies on semicontinuous pellet feeding during oxidation, the use of 40% oxygen instead of lower oxygen concentrations, and fuel element decladding.

Semiworks Plant Tests

Twelve new runs (UE-43 through -54) were conducted using annular EGCR or solid cylindrical Westinghouse uranium dioxide pellets, a PRTR fuel element, and an ORGDP-fabricated simulated fuel element. Alcoa tabular alumina was the bed diluent in all tests.

Several factors of possible influence on U_3O_8 elutriation during oxidation were studied. These included hydrogen chloride pretreatment of EGCR pellets, length of exposure to hydrogen chloride, and superficial velocity during oxidation.

A cold "normal" assay PRTR fuel element containing eighteen zircaloy-clad fuel rods and the second sixty-tube simulated fuel element fabricated in ORGDP shops were processed through decladding and oxidation. The PRTR test was the first in the semiworks plant with an actual reactor fuel assembly.

A series of runs featured semicontinuous pellet feeding during oxidation. In these runs, the pellets were fed to the reactor through a hold volume attached to the charging port at the top of the reactor. This mode of feeding is considered possibly applicable when preceded by a mechanical decladding process from which uranium dioxide pellets would be available for subsequent processing. Semicontinuous feeding of alumina to the filter cooler and removal of fluid-bed powder from the cooler during the oxidation process were also attempted.

In some of the oxidation tests, 40% oxygen was used instead of 21%. Westinghouse pellets and EGCR pellets were oxidized in separate runs to uncover possible differences in results at this high concentration.

The same six filters which had been in use in most of the semiworks operation since the start of the program were used again in these tests. The filters were washed once during the test period to maintain permeability.

The current tests indicated the following:

1. The rate of U_3O_8 elutriation is increased by pellet exposures to hydrogen chloride of as little as 1 hour prior to oxidation, by raising the superficial velocity from 1.5 to 2.4 ft/sec, and by the use of 40% oxygen instead of concentrations in the range of 11 to 21% oxygen. Since U_3O_8 elutriation rates in excess of 7 kg per 1,000 scf of gas, deemed necessary for a plant operation, have been achieved; elutriation is probably a practical transfer technique for the two-vessel process.

2. The PRTR fuel element and the simulated fuel element were successfully processed in the semiworks reactor. Unreacted end caps and fragments of fuel cladding did not interfere with oxidation in the test with the PRTR fuel element.

3. When uranium dioxide pellets are fed semicontinuously to a fluid-bed reactor during oxidation, the temperature and pressure drop increases can be controlled and bed performance is not upset.

4. A concentration of 40% oxygen in nitrogen can be used from the outset of oxidation in shallow pellet beds. Vibration might be necessary to control high pressure drop buildup across the beds. The oxidized product with EGCR pellets appears to be fine enough for fluid-bed fluorination.

5. The comminution of solid Westinghouse pellets to minus 35-mesh particles is poorer than that obtained with cylindrical EGCR pellets when usual oxidation procedures are used. The differences might not be so pronounced with irradiated fuel processing.

In summary, the overall reactor system studies have indicated that (1) the removal of zircaloy cladding by reaction with hydrogen chloride proceeds satisfactorily and at sufficient rates for most purposes; (2) oxidation of uranium dioxide pellets can be performed satisfactorily, providing the proper gas velocity is employed and the reaction zone is located close to the top of the pellet zone; (3) fluid-bed fluorination with elemental fluorine can be performed readily at temperatures of 350 to 400°C and probably higher; and (4) a significant heat release will occur in the elemental fluorine fluorination step because of the failure of bromine pentafluoride to convert completely some of the fission product elements.

Outlet Filter Gas Studies

Studies were continued in the filter test loop in search of the cause of and a remedy for the plugging of sintered nickel fiber filter tubes in declad reaction off-gases. Activities were centered on the volatilization of zirconium tetrachloride from zircaloy tetrachloride powder charges to the reactor with hydrogen and with hydrogen and hydrogen chloride in the fluidizing gases. In addition, a 316 stainless steel filter was exposed to declad reaction off-gases; this material had been proposed for the filtration of the off-gases from the declad and oxidation steps in a two-reactor process.

The exposure of zirconium tetrachloride plus a mixture of 30% hydrogen and 70% oxygen-free argon resulted in about a 20% permeability loss in the sintered nickel fiber filter; while hydrogen chloride, zirconium tetrachloride, and argon, with or without hydrogen, plugged the filter beyond satisfactory use, i.e., greater than 95%. The permeability loss for the stainless steel filter over the course of thirteen exposure cycles was likewise greater than 95%.

While the filter tube for general use with the fluoride volatility process has not been found, the use of separate filters for the operational steps might be desirable. For example, based on past corrosion tests, it might be possible to use stainless steel filters for chemical decladding and oxidation, while the fluorination off-gases would be routed through nickel filters.

Product Purification Sorption-Desorption Tests

New studies were made to cover high gas flow, low uranium hexafluoride concentration cases, such as might be encountered with exhaust gases from a cold trap backup system or to a sorption system in the event of a dilute gas release. The results indicate that an operating temperature of $93 \pm 8°C$ should be satisfactory at a velocity of 1 ft/sec and a 200 ppm uranium hexafluoride concentration to reduce the outlet gas concentration to about 4 ppm. Since a bias might have been present during testing due to uranium hexafluoride background in the test system, it is possible that still lower outlet concentrations might be achievable.

PERIPHERAL COMPRESSOR

After 3,813 hours of operation, the compressor was shut down to replace bearings which were overheating. The bearing set nearest the compressor motor was found to have been damaged as the result of the degradation of the lubricating qualities of the grease. The bearings had performed well beyond the expected 2,500-hour life.

It is concluded that this compressor is potentially suited for the recycle of fluoride volatility process reagent gases.

DISCUSSION

ENGINEERING STUDIES

D. L. Breton, D. I. Dunthorn, K. E. Habiger,
J. R. Merriman, T. H. Monk

In keeping with the close-out plan for the Oak Ridge Gaseous Diffusion Plant fluoride volatility program, program engineering studies were concluded during this period. During the final report period, the conceptual processing plant study for light water fuels was completed; engineering calculations associated with that study and scoping calculations for the volatility reprocessing of spent FBR, i.e., Fast Breeder Reactor, fuels were made; and topical reports on (1) the design of cold traps, (2) nuclear safety studies for plants reprocessing high and low enrichment fuels, and (3) the conceptual plant engineering evaluation were prepared for publication.

CONCEPTUAL PLANT STUDIES

The completed report on the conceptual plant study contains sections on the bases for the work, process technology, process description, process critique, general facilities, safety, plant staff, costs, and conclusions and recommendations. The process rate was established at 1-tonne of uranium per day with the corresponding daily plutonium process rate being 9.7 kg. Conceptual drawings for important process equipment items are included, as well as layouts for fuel receipt and waste storage areas, process cells, and plant buildings. Since plutonium purification technology was not available, space and cost allowances, deemed adequate, were made for this portion of the process.

The plant is located on a 200-acre site. Staff requirements are 119 people. The facility includes (a) a process building with a total floor area of 46,500 sq ft, including a process cell area of 2,650 sq ft; (b) a fuel receipt building of 8,770 sq ft; (c) a cell and process gas filtration system and a 400-foot-tall stack; (d) a 23,000 sq ft utility, maintenance, and fluorine plant building; (e) an 8,000 sq ft warehouse; (f) waste storage areas; and (g) the usual utility and general improvements associated with process plants.

The capital cost of the plant has been estimated to be 33 million dollars with a 25% contingency included. With a depreciation charge of 15% per year, the unit capital charge becomes $16.34 per kilogram of uranium. The operating cost is estimated to be $10.98 per kilogram of uranium. The total unit fuel reprocessing cost would be the sum of the two, i.e., $27.32 per kilogram. It should be stressed that, since the study was conceptual in nature, sufficient manpower and funding were not expended to prepare designs and layouts in sufficient detail to achieve high precision in the cost estimate.

FBR CALCULATIONS

The FBR scoping calculations were made to aid in assessing the applicability of the process to the treatment of irradiated fuels. The work was performed in cooperation with Argonne National Laboratory and was aimed at providing input information for their FBR fuel reprocessing studies. Calculations were made in five general areas. They were (1) the economics associated with alumina bed reusage, (2) static bed temperature increases due to radioactive heat generation, (3) the transfer of fission product heat from fluid-bed reactors, (4) the reagent requirements for plutonium fluorination, and (5) nuclear safety.

For the FBR calculations, it was assumed that the fuel assembly charged to the volatility process is comprised of 50% core material (20% plutonium dioxide-80% uranium dioxide) and 50% axial blanket material. Average FBR assembly radioactive heat generation rates were computed based on this split, assuming a core burnup and a specific power of 100,000 Mwd/tonne and 200 Mw/tonne, respectively; the axial blanket burnup and specific power were assumed to be 6,600 Mwd/tonne and 13.2 Mw/tonne, respectively. The average decay heats at various cooling times are shown in table I.

TABLE I

RADIOACTIVE DECAY HEAT FOR SPENT FBR FUEL

Cooling Time, days	Decay Heat*, Btu/hr-kg (U + Pu)		
	Core	Blanket	Average†
10	1,461	97	779
20	1,104	73	588
30	903	60	482
60	607	40	324
90	465	31	248
120	375	25	200
180	281	17	139

* Core burnup = 100,000 Mwd/tonne; specific power = 200 Mw/tonne; Blanket burnup = 6,600 Mwd/tonne; specific power = 13.2 Mw/tonne.

† 50% core and 50% blanket.

Discussions of the calculations are presented in the following paragraphs.

Alumina Usage Economics

A few calculations were made to assess the bed diluent usage economics. The bed material was assumed to be alumina, and the computed utilization costs included alumina costs, plutonium loss charges, and waste storage investment based on bin storage costs developed at the Idaho Chemical Processing Plant*. The computed values are listed in table II for 30- and 120-day cooled fuel. The independent variable for these calculations was the alumina usage ratio; i.e., the kilogram quantity of alumina used per kilogram of uranium plus plutonium processed.

The cost of the alumina was taken as $0.19 per pound, and the penalty for the plutonium losses was set at $10 per gram. Plutonium retention on the discharge alumina was assumed to be 0.03 weight percent†. The results, in general, indicate that reduction of the alumina usage, perhaps by recycle, is desirable from an economic standpoint, as might be expected. They also show that storage capital costs are of the same order of magnitude as the value of plutonium losses. It should be noted that bin storage costs for bin thicknesses less than 3.0 inches were not available, so that the extrapolations to lesser thicknesses may be questionable.

The results also indicate that some storage cost savings may be obtained by processing longer cooled fuel; however, interestingly enough, this savings apparently is not large enough to be economically controlling in the cases studied. If processing of longer cooled fuel permitted reduction in waste volume, e.g., by allowing more recycles than possible with shorter cooled material, the economic significance would be greater.

Figure 1 shows the resultant volumetric heat generation rate in the waste alumina as a function of the alumina usage ratio, with cooling time as a parameter. The alumina density was taken to be 135 pounds per cubic foot. The bin thicknesses required to maintain a centerline-to-wall temperature difference of 650°C are indicated on the plot; they were calculated assuming a slab geometry and an alumina thermal conductivity of 0.2 Btu/hr-ft-°F.

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* Stevens, J. I., An Economic Evaluation of Ultimate Disposal of Liquid Radioactive Wastes by the Fluidized Bed Calcination Process, Phillips Petroleum Company, October 30, 1962 (IDO-14595).

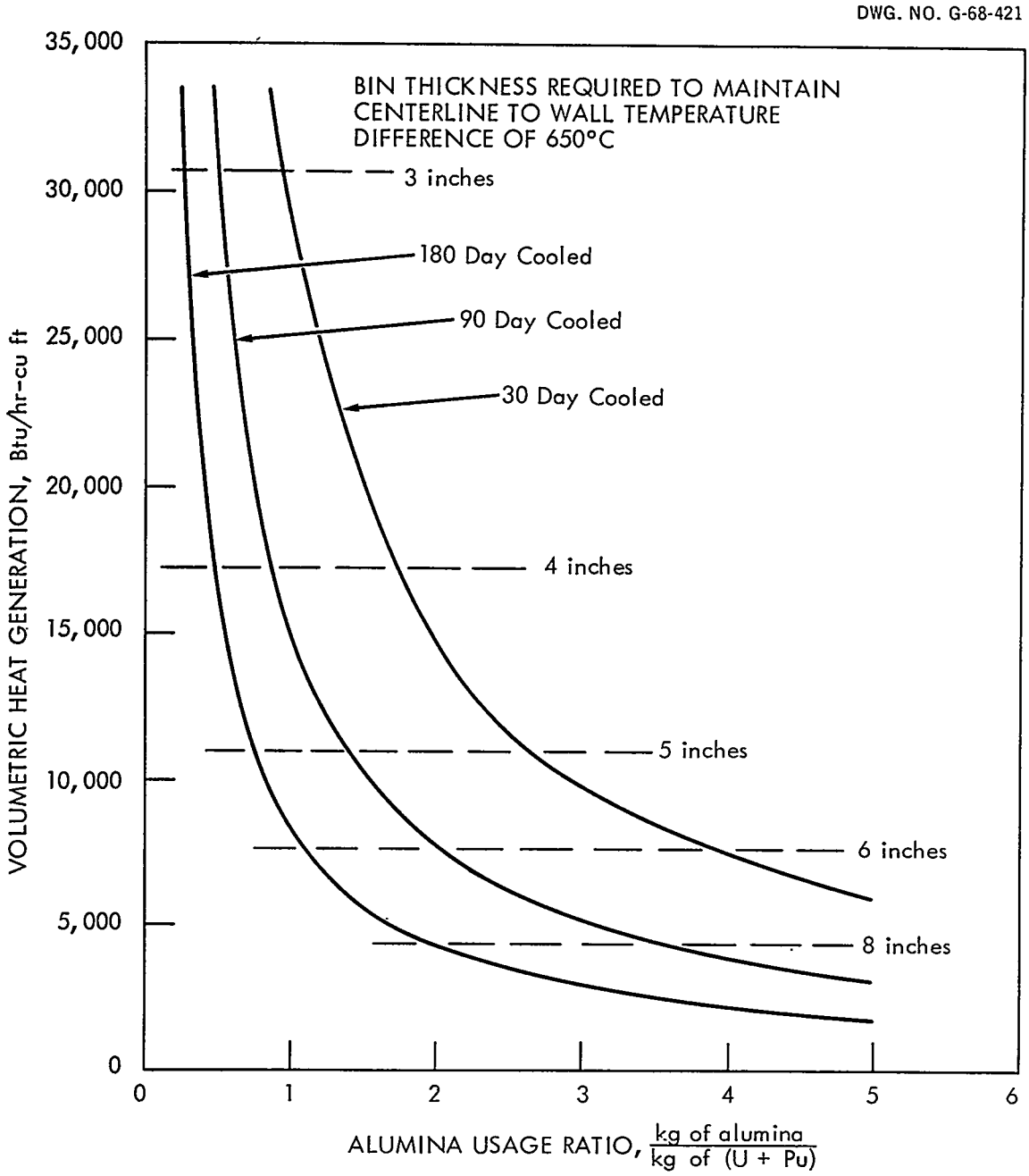
† The 0.03% plutonium retention value, although somewhat higher than average holdups experienced at ANL during treatment of dilute plutonium mixtures, was chosen on the basis of the high plutonium concentrations in FBR fuel charges.

TABLE II

ALUMINA USAGE ECONOMICS
IN PROCESSING SPENT FBR FUEL

Alumina Usage Ratio*	Bin Thickness, inch	Costs, $/kg (U + Pu)			
		Waste Storage	Plutonium Losses	Alumina	Total
Cooling Time = 30 days					
0.25	1.54	0.92	0.75	0.10	1.77
0.50	2.16	1.01	1.50	0.21	3.32
1.00	3.06	2.77	3.00	0.42	6.19
2.00	4.33	4.74	6.00	0.84	11.58
3.00	5.32	6.48	9.00	1.26	16.74
4.00	6.11	8.11	12.00	1.67	21.78
5.00	6.84	9.65	15.00	2.09	26.74
Cooling Time = 120 days					
0.25	2.38	0.77	0.75	0.10	1.63
0.50	3.36	1.33	1.50	0.21	3.04
1.00	4.76	2.27	3.00	0.42	5.69
2.00	6.73	3.89	6.00	0.84	10.73
3.00	8.21	5.35	9.00	1.26	15.61
4.00	9.44	6.72	12.00	1.67	20.39
5.00	10.73	7.97	15.00	2.09	25.06

* The alumina usage ratio is the kilogram quantity of alumina used per kilogram of uranium plus plutonium processed.



WASTE ALUMINA
VOLUMETRIC HEAT GENERATION RATE

Figure 1

Static Bed Temperature Increases Due to Radioactive Heat Generation

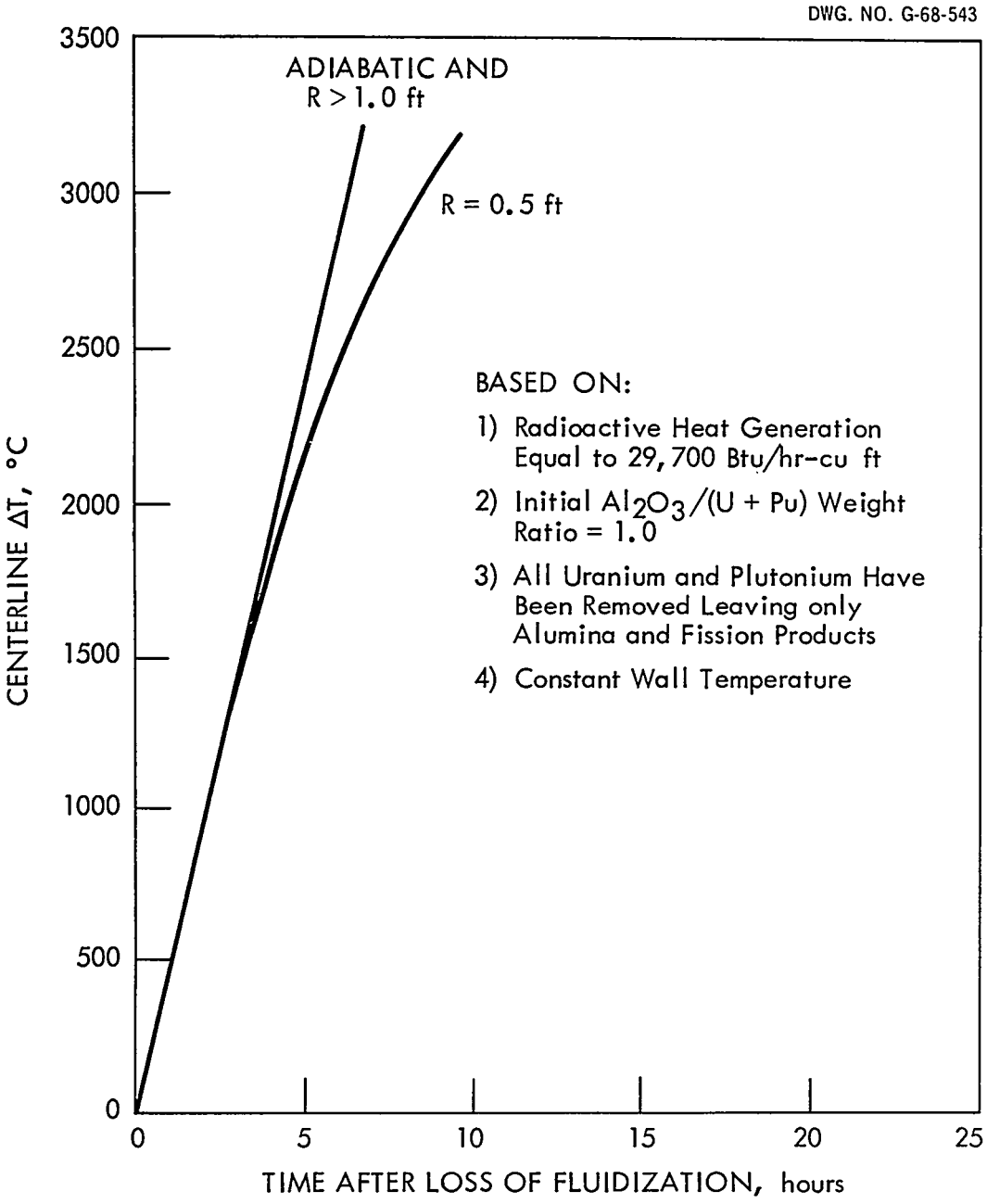
If fluidization were lost in a head-end reactor during processing, fission products present in the settled bed would cause heating which, if not checked, could eventually increase bed temperatures to the point where sintering or even melting of the contents could occur. Since this is an area of considerable concern, due to the possibly great difficulties which might be involved in removing plugs in an operating plant, estimates were made of the temperature increase rates which might be encountered for several FBR fuels. From these rates, estimates can be made of downtime before effective corrective action need be taken. These estimates would tend to be conservative, since it is probable that some gas could be passed through a plugged bed and with resultant increase in heat removal rate.

In this respect, it should be noted that the upper temperature permissible in the static bed is likely to be more a function of the caking tendencies of the minor constituents, i.e., fission product compounds, present rather than the caking tendencies of the relatively refractory aluminum oxide. Of course, tests to establish temperature limits for typical bed mixtures would certainly be valuable in setting the limits on the allowable static bed downtime. The results of the calculations described in the following sections should, however, provide approximate guides and comparisons for cylindrical and annular design cases.

Solid Cylinders Containing Fission Products Only. Calculations were made to estimate the centerline temperature rise rates of settled cylindrical alumina beds containing fission products from high burnup breeder reactor fuels. These calculations were made for the case where fluidization is lost immediately after removing all plutonium and uranium from the bed, with only alumina and fission products left behind. This should be the most conservative case, since, for initial alumina-to-fissile material weight ratios of 1, the volumetric heat generation rates are approximately doubled when the fissile material is removed.

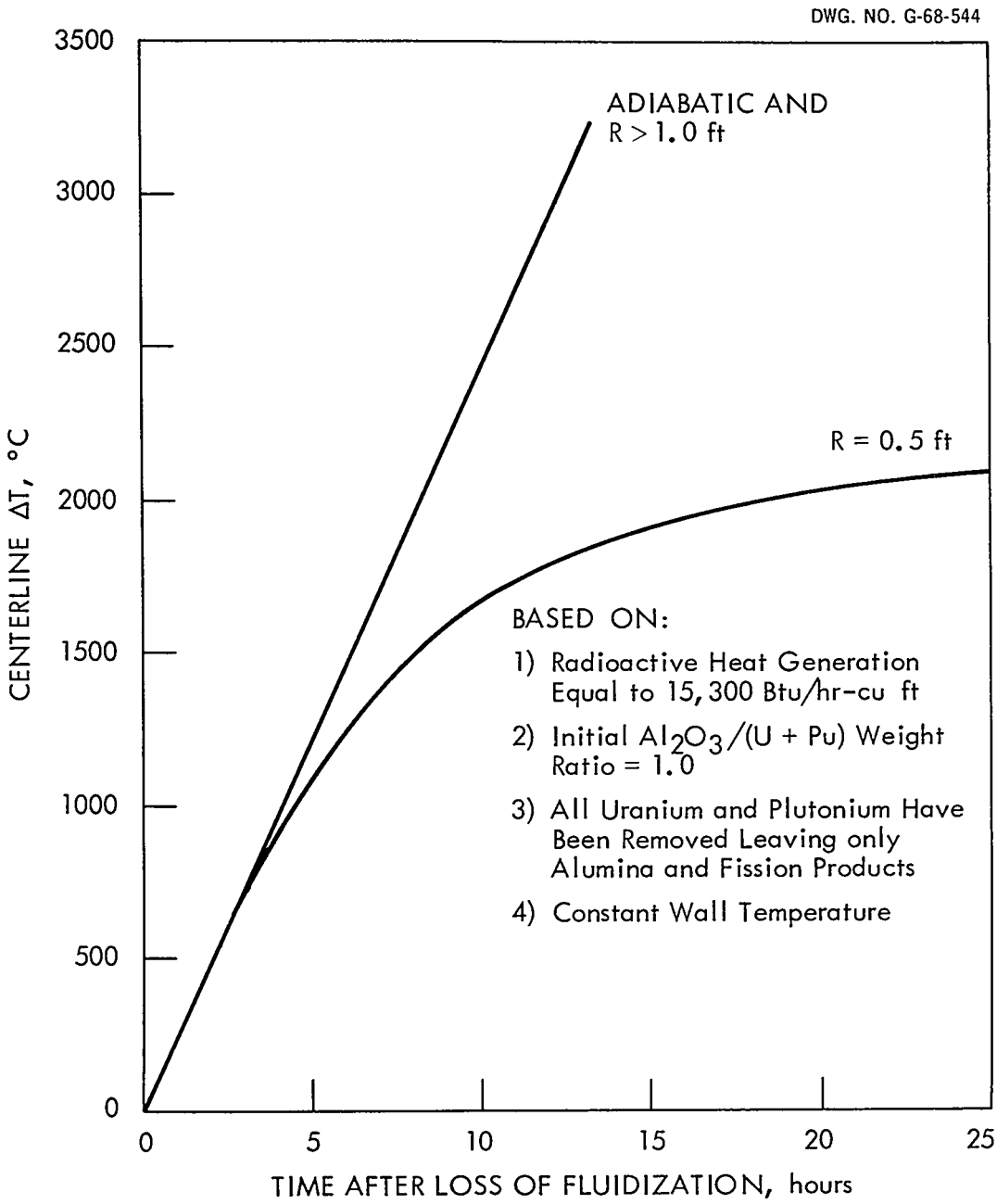
The bed density, heat capacity, and thermal conductivity were taken to be 135 lb/cu ft, 0.26 Btu/lb-$^{\circ}$F, and 0.26 Btu/hr-ft-$^{\circ}$F, respectively. The initial ratio of alumina to fuel prior to fluorination was assumed to be unity, and it was assumed that the wall temperature could be held at its initial value. The results of the calculations are shown in figures 2 through 4 for cooling times from 30 to 180 days and for bed radii of 0.5, 1.0, and 1.5 feet.

Annular Cylinders Containing Fission Products Only. For comparison purposes, calculations were repeated for annular cylinders to estimate the maximum temperature rise rates of settled beds, again containing no uranium or plutonium. The values for bed density, heat capacity, and thermal conductivity were those which were used for the solid cylinder cases, and the starting bed alumina-to-feed ratio was once more taken as 1.0. Annulus dimensions of 3, 4, 6, and 8 inches were considered



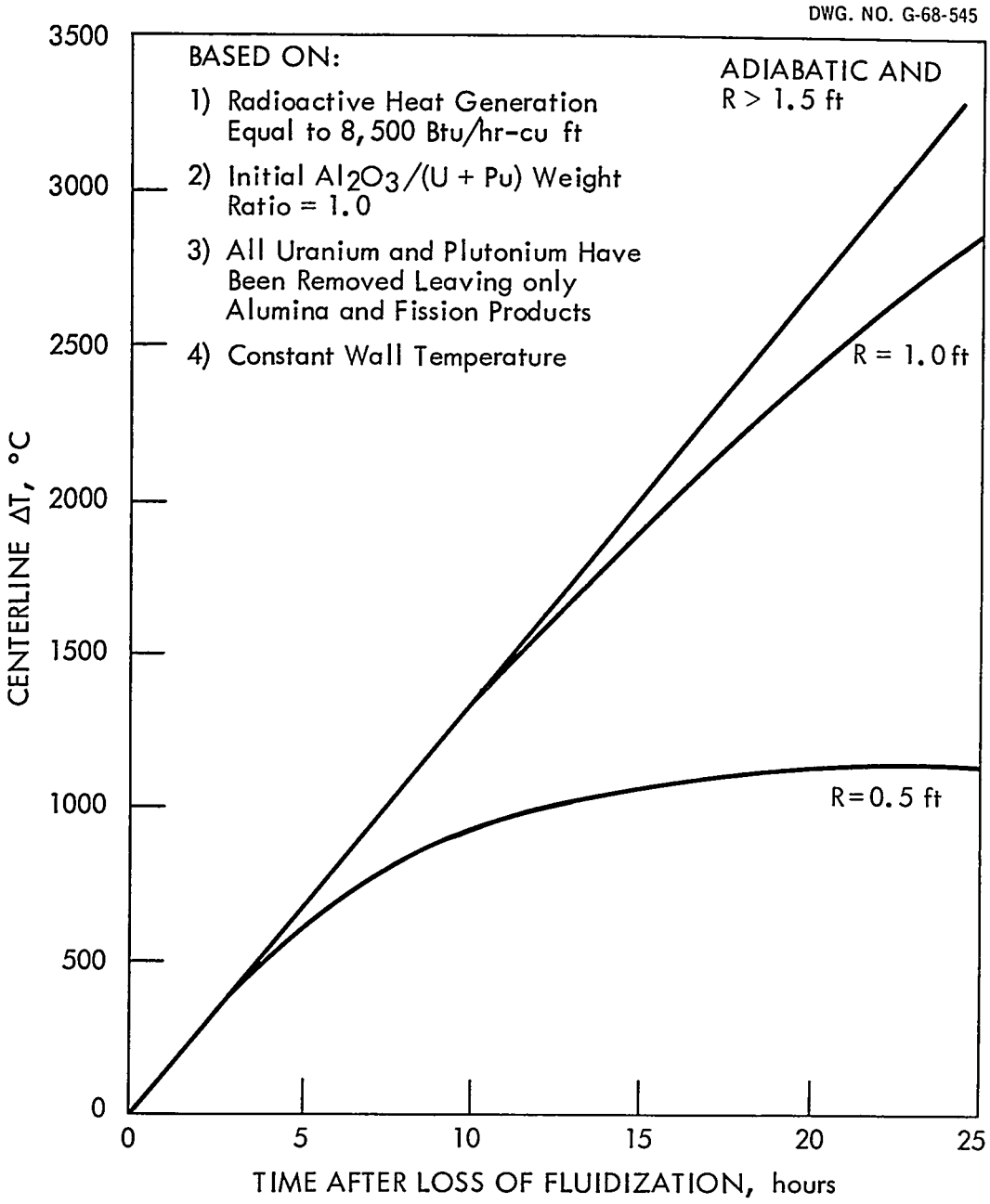
CENTERLINE TEMPERATURE RISES FOR
SETTLED ALUMINA BEDS IN CYLINDRICAL VESSELS
CASE I: FUEL COOLED 30 DAYS

Figure 2



CENTERLINE TEMPERATURE RISES FOR
SETTLED ALUMINA BEDS IN CYLINDRICAL VESSELS
CASE II: FUEL COOLED 90 DAYS

Figure 3



CENTERLINE TEMPERATURE RISES FOR
SETTLED ALUMINA BEDS IN CYLINDRICAL VESSELS
CASE III: FUEL COOLED 180 DAYS

Figure 4

using central diameters of 4, 8, and 12 inches for each annular thickness. It was observed that temperature rises for a given annulus thickness were about the same for all of the central diameters considered at that thickness; accordingly, the results for the 4-inch-inside-diameter cases are the only ones presented here. Values for the other inside diameters considered differ from the plotted values by less than 5%. The results are shown in figures 5 through 7 for reference fuel cooling times of 30, 90, and 180 days.

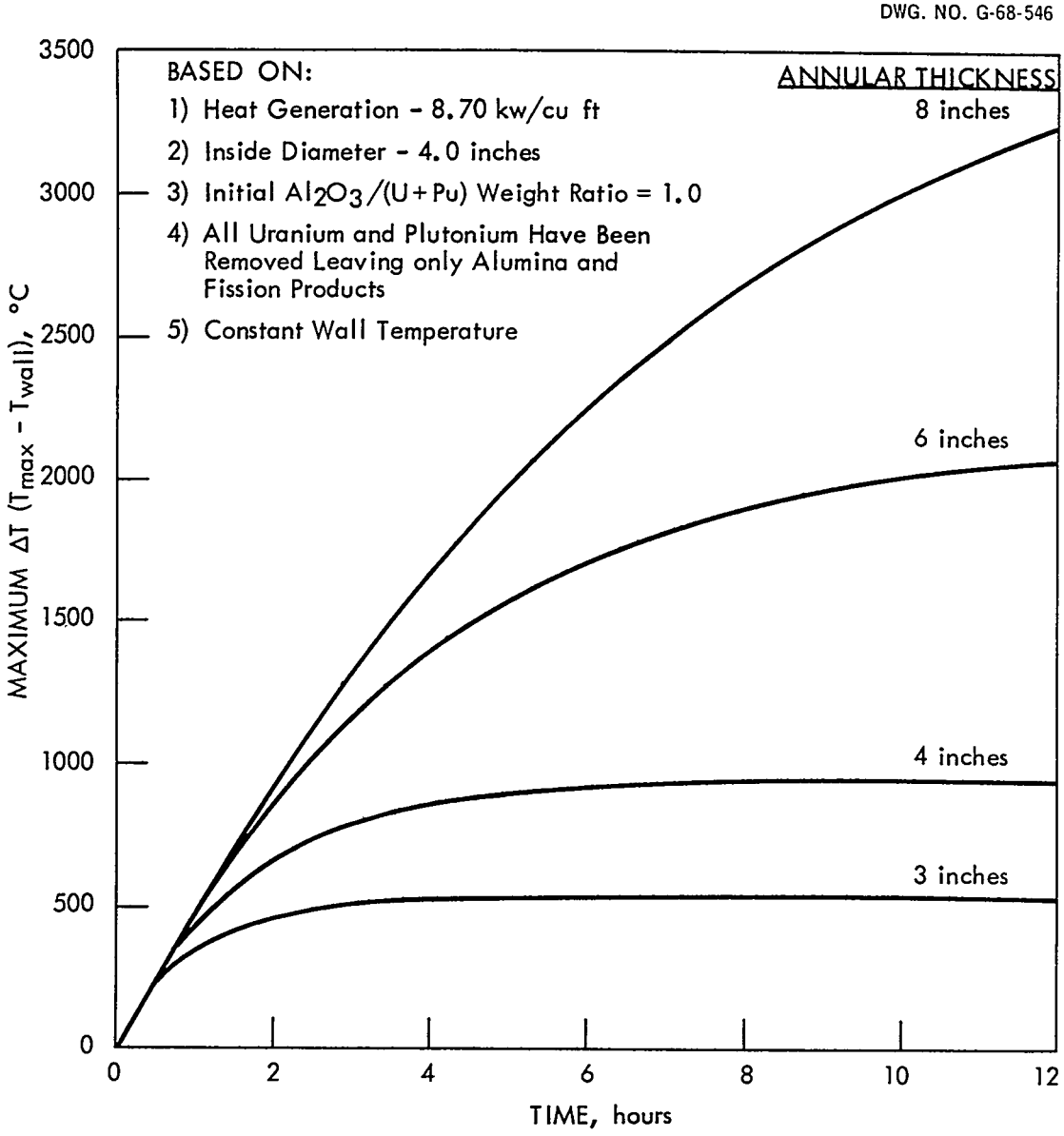
Comparing figures 2 through 4, it can be seen that, for a 1-foot-diameter cylindrical reactor, a centerline-to-wall temperature difference of 800°C is reached in about 1.8 hours when the fuel has been cooled 30 days before processing. With an annular reactor having a 4-inch-inner pipe diameter, an annulus thickness of about 4.3 inches is required to achieve the same flow area as in the cylindrical case. For this annulus size, the 800°C temperature difference is not reached until after about 3 hours. This advantage can be increased by going to inside pipe sizes larger than 4 inches and, consequently, to smaller annulus thicknesses for the same cross sectional area; however, other considerations, primarily throughput demands and operational feasibility, limit the extent to which the annular thickness can be reduced.

Transfer of Fission Product Heat from Fluid-Bed Reactors

The burnup for fast breeder fuels will be considerably greater than the burnup for low enrichment LWR fuels. Consequently, fission product heat releases will necessitate more fluid-bed cooling capacity than envisioned for thermal reactor fuel plants. In fact, for very large diameters, the cooling requirements for removing the fission product decay heat alone, neglecting chemical reaction heat, may not be practical for high throughputs.

Table III shows typical heat fluxes required for removing fission product heat for four different volumetric heat generation rates. The volumetric heat generation rate is dependent on both the alumina usage and the fuel cooling time.

As presented earlier in figure 1, volumetric heat generation rates as high as 30,000 Btu/hr-cu ft are possible at low alumina usage ratios. Considering table III, then, it can be seen that, for several reactor sizes, the heat fluxes required to remove this amount of fission product heat are less than 15,000 Btu/hr-sq ft of wall area. Since fluid-bed heat fluxes in the range of 10,000 to 15,000 Btu/hr-sq ft can be achieved with a properly designed cooling system, fluid-bed reactor diameters up to 24 inches seem practical from the heat transfer standpoint. It should be pointed out, however, that other limitations may require use of smaller diameter reactors. For example, the quantity of plutonium contained in a 24-inch-diameter reactor would be about 43 kg, assuming a 6-foot bed depth and equal amounts of alumina and reference fuel material. Under certain conditions, this mass of plutonium could be critical, e.g., for plutonium dioxide at a powder density of 4.5 g/cc with 30 cm of alumina



TRANSIENT TEMPERATURE RISE IN STATIC ANNULAR BED
CASE I: FUEL COOLED 30 DAYS

Figure 5

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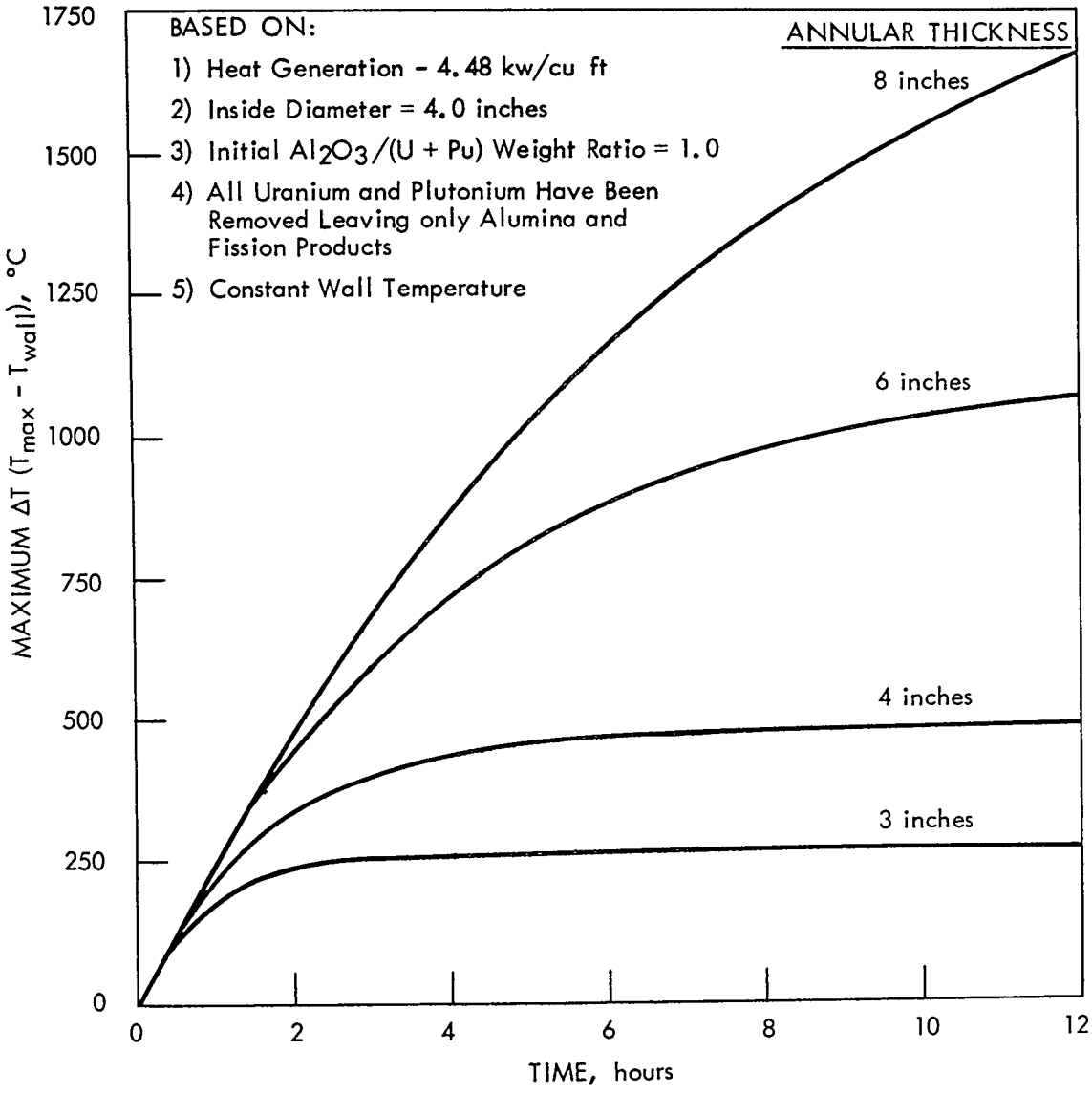

TRANSIENT TEMPERATURE RISE IN STATIC ANNULAR BED
CASE II: FUEL COOLED 90 DAYS

Figure 6

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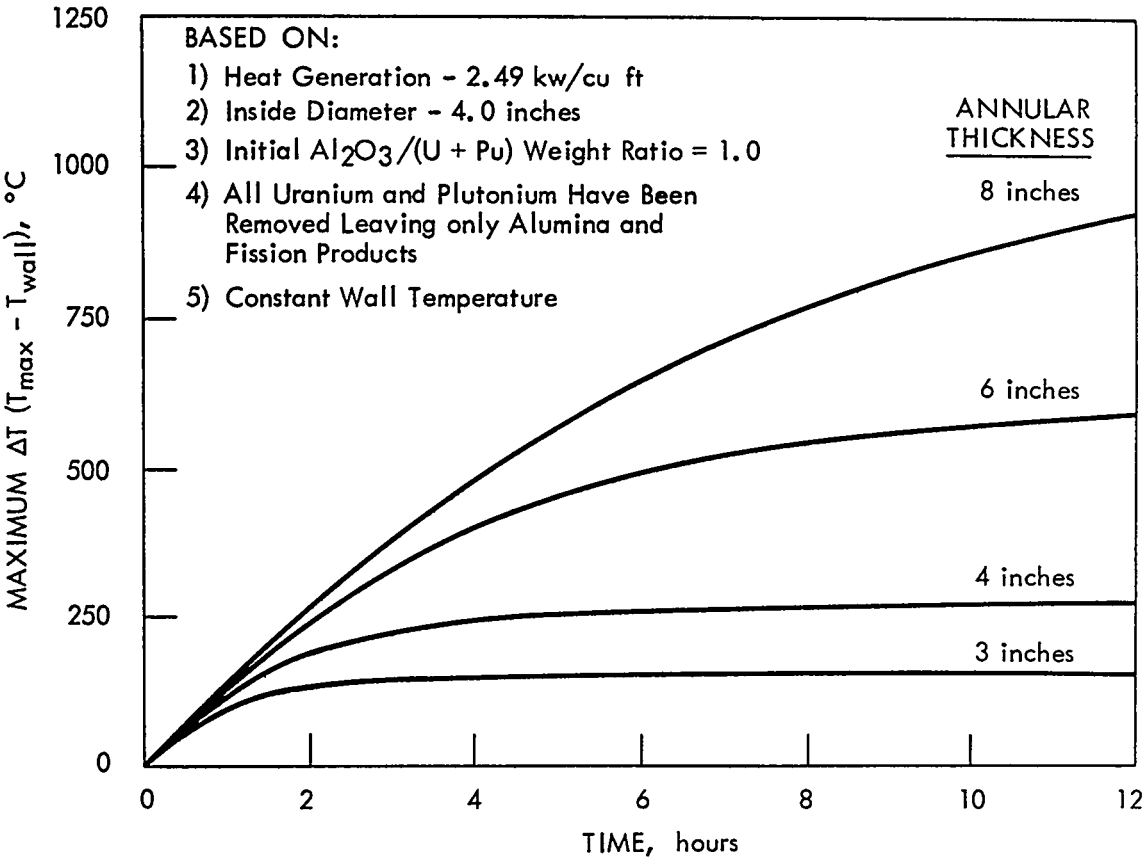

TRANSIENT TEMPERATURE RISE IN STATIC ANNULAR BED
CASE III: FUEL COOLED 180 DAYS

Figure 7

TABLE III

FLUID-BED HEAT LOADS RESULTING FROM FISSION PRODUCT HEAT

Reactor Diameter, inch	Heat Flux at Indicated Volume Heat Generation Rates, Btu/hr-sq ft of reactor wall			
	10,000 Btu/hr-cu ft	15,000 Btu/hr-cu ft	20,000 Btu/hr-cu ft	30,000 Btu/hr-cu ft
6	1,250	1,880	2,500	3,800
9	1,870	2,810	3,750	5,600
12	2,500	3,750	5,000	7,500
15	3,120	4,690	6,250	9,400
18	3,750	5,630	7,500	11,300
24	5,000	7,500	10,000	15,000

reflection, the critical spherical mass of plutonium has been computed* to be in the range of 38 to 41 kg for the plutonium isotopic compositions arising from irradiation levels of 10,000 to 30,000 Mwd/tonne of uranium.

Plutonium Fluorination Requirements

In fast breeder fuels, the plutonium concentration at discharge is much higher than that for thermal fuels. Since the fluorination of plutonium tetrafluoride requires large quantities of fluorine, due to equilibrium limitations, the time requirements for processing large quantities of plutonium are of considerable interest. For scoping purposes, plutonium hexafluoride production capabilities for various diameter reactors were calculated by assuming that the product gases contained equilibrium proportions of plutonium hexafluoride and fluorine at the fluid-bed operating temperature. The results are plotted in figure 8. A gas velocity of 1.0 ft/sec and a pressure of 1 atmosphere of fluorine were assumed. The fluorination rates presented in figure 8 are for continuous operation of a reactor; however, semicontinuous or batch processing of the plutonium will probably be the route actually taken in the plutonium processing step. Semicontinuous or batch processing rates will, of course, be less than the rates predicted for continuous processing. Therefore, in an attempt to establish limits for the plutonium processing rate, calculations were also made for batch processing. Here, the bed temperature was assumed to be 300°C initially; upon beginning the plutonium fluorination step, the bed temperature was allowed to increase to 400°C at a rate of 20°C/hr. During the latter stages of batch fluorination when the plutonium concentration in the fluid bed becomes small, the off-gases leaving the bed will probably no longer contain plutonium hexafluoride and fluorine at their equilibrium ratio; it is likely that the plutonium hexafluoride-to-fluorine ratio would be less than the equilibrium value, and fluorination would require increased quantities of fluorine.

Data from ANL experiments on plutonium fluorination have been used to estimate the degree of equilibrium attained as a function of the plutonium concentration in the bed; the results are plotted in figure 9. The independent variable is the ratio of the moles of plutonium charged to the initial molar flow rate of fluorine (moles per hour), i.e., at 300°C. The fluidizing velocity is maintained at a constant value throughout the operation as the bed temperature is increased from 300 to 400°C at 20°C/hr. The parameter is the initial mass ratio of plutonium to alumina. Fluorine requirements are then expressed as the moles of fluorine required to fluorinate one mole of plutonium (tetrafluoride) with 99% plutonium recovery.

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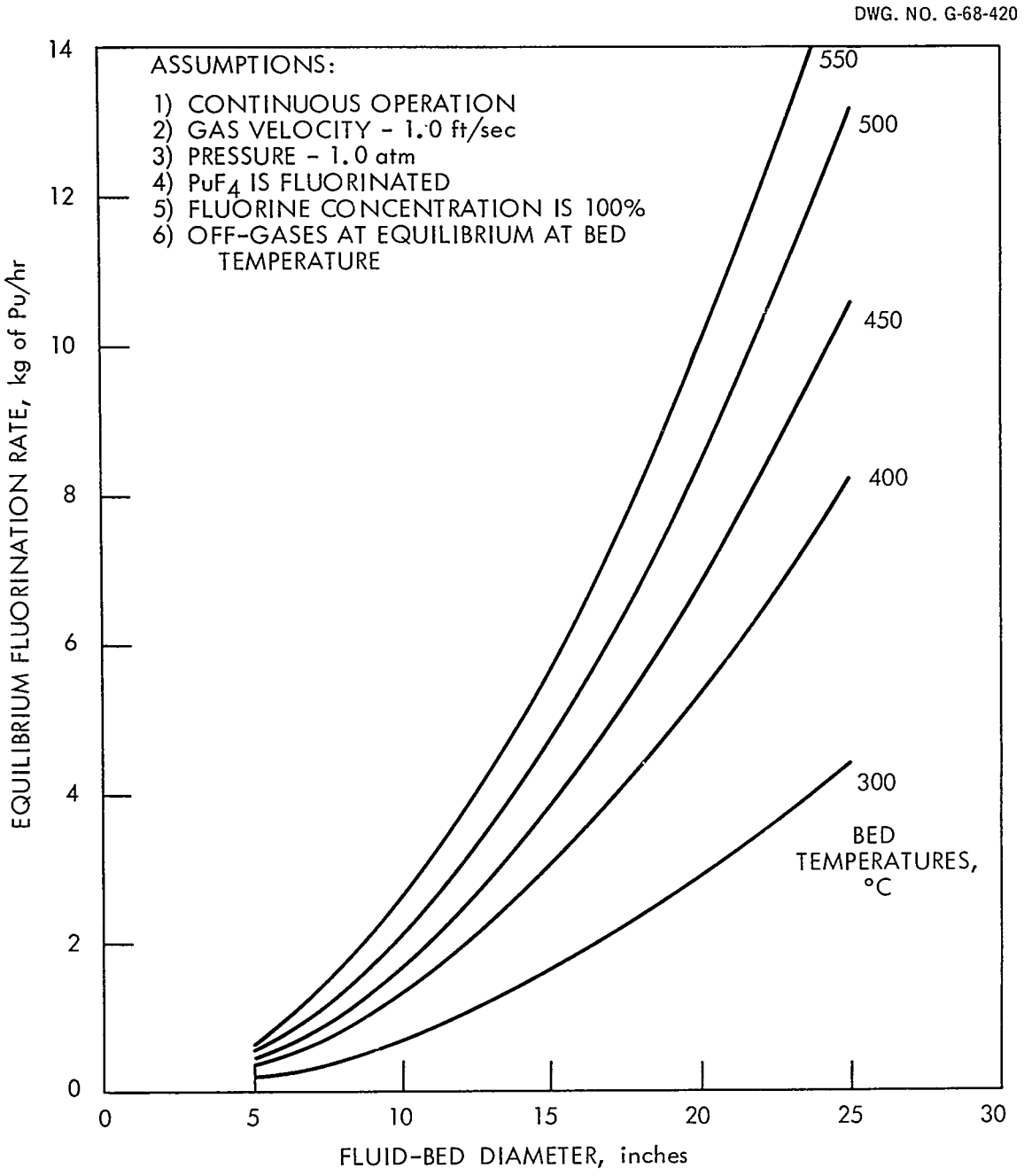
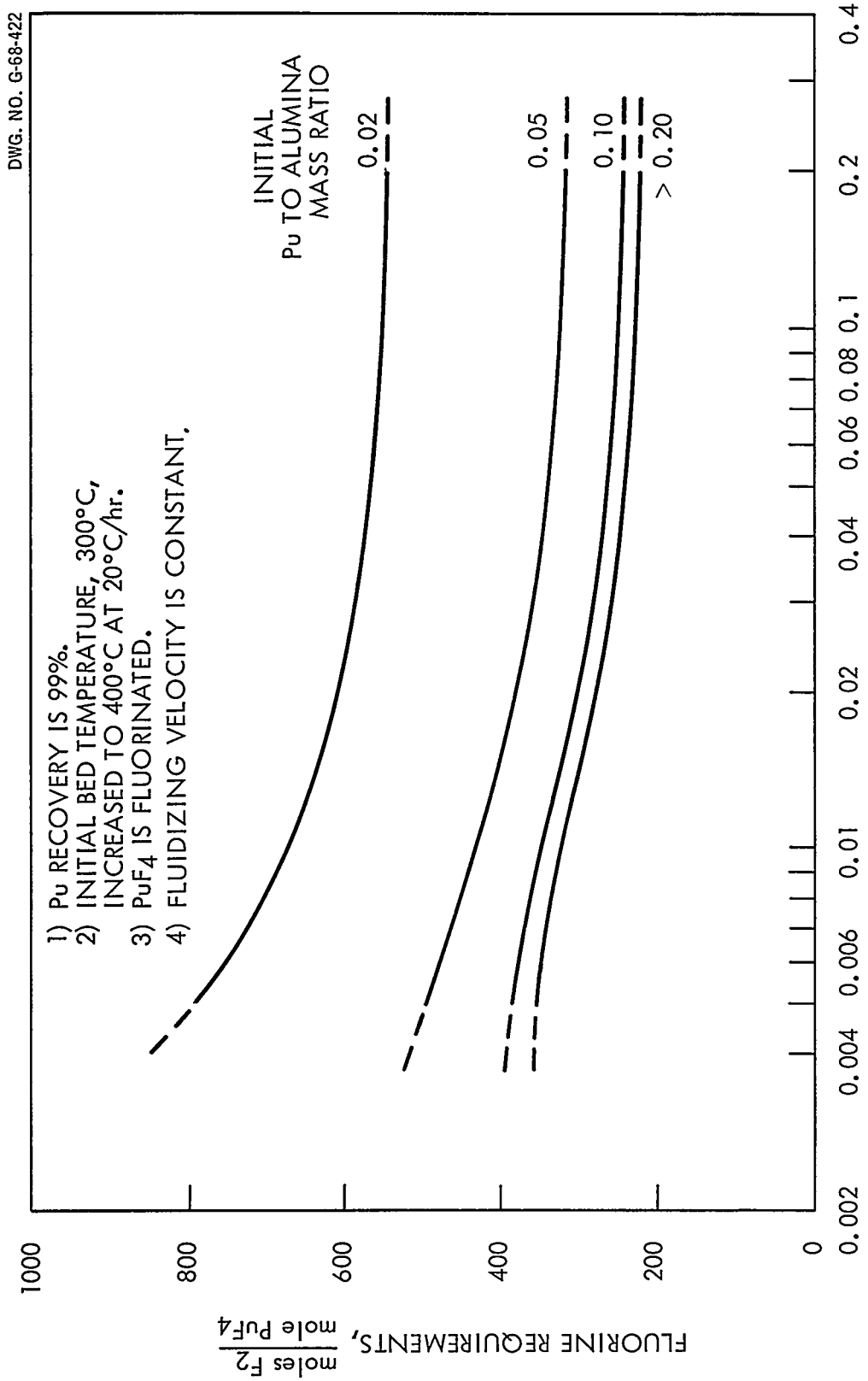
* Smiley, S. H., Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report January through June, 1966, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, January 18, 1967 (K-1691), p. 36.



CONTINUOUS PLUTONIUM FLUORINATION AS A FUNCTION OF BED DIAMETER

Figure 8



PLUTONIUM BATCH FLUORINATION

Figure 9

As an example of the use of figure 9, consider a 12-inch-diameter reactor with a 6-foot bed operated at a gas velocity of 1.0 ft/sec, a system pressure of 1 atmosphere, and an alumina usage ratio of 1.0; i.e., one kilogram of alumina used per kilogram of uranium plus plutonium processed. These values correspond to a plutonium charge of approximately 9.4 kg, a molar ratio of plutonium charge to fluorine flow at 300°C of 0.02317 hour, and an initial mass ratio of plutonium to alumina of 0.0822. From figure 9, the moles of fluorine required per mole of plutonium tetrafluoride reacted is 310. The fluorination time will be 310 times 0.02317, or 7.2 hours, and the average fluorination rate will be about 1.3 kg of plutonium per hour. As a comparison, the fluorination time for the 9.4 kg plutonium charge would be 4.7 hours if equilibrium at 400°C were maintained through the fluorination step (figure 8). The fluorination rate for the equilibrium case would be about 2 kg/hr.

Nuclear Safety

The handling of FBR fuels poses difficult nuclear safety problems for a reprocessing plant treating sizable fuel loads, because of the large quantities of plutonium contained in the fuel. Even with its general advantage over aqueous schemes because of the absence of hydrogen moderation, the fluoride volatility process for FBR fuels is, nevertheless, faced with equipment size and batch limits which require considerable ingenuity on the part of the design engineer. To provide input for the FBR studies, then, several calculations have been made to ascertain the nuclear reactivities of several plutonium processing reactor designs; the cases studied have involved both plutonium dioxide and plutonium tetrafluoride, at various densities, containing in spheres, infinite cylinders, infinite annuli, infinite slabs, finite cylinders, and finite slabs.

Spheres and Infinite Cylinders. Critical radii for infinite cylinders and for spheres containing homogeneous mixtures of plutonium dioxide and alumina, and also plutonium tetrafluoride and alumina have been estimated using the ANISN neutron transport code. Presented in tables IV through VII, the results are also shown in figures 10 through 13 for easier inspection.

It was assumed for all cases that the cylinders or spheres were reflected with 30 cm of alumina. The alumina density, both in the reflector and in the fuel mixture was taken to be 2.5 g/cc. Fissile material compound densities assumed were 5, 6, and 9 g/cc for the oxide calculations and 3, 5, and 7 g/cc for the fluoride cases*. All plutonium was considered to be plutonium-239. Additionally, it was assumed that volumes of fissile

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* These calculations are extensions of previous work summarized in tables A-VII and A-VIII of the ORGDP report: Habiger, K. E., and Breton, D. L., Nuclear Safety Studies for Low Enrichment Fluoride Volatility Fuel Reprocessing Plants, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, September 4, 1968 (K-1734).

TABLE IV

CRITICAL RADII FOR INFINITE CYLINDERS
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM DIOXIDE AND ALUMINA*

Plutonium Dioxide, volume percent	Plutonium, weight percent	Critical Radius, cm
Plutonium Dioxide Density = 9 g/cc		
10	25.20	18.54
40	62.25	7.58
70	78.81	5.16
100	88.19	4.02
Plutonium Dioxide Density = 6 g/cc		
10	18.57	23.54
40	54.27	10.07
70	74.82	6.94
100	88.19	5.44
Plutonium Dioxide Density = 5 g/cc		
10	16.03	26.21
40	50.40	11.44
70	72.63	7.92
100	88.19	6.22

* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.

TABLE V

CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM DIOXIDE AND ALUMINA*

Plutonium Dioxide, volume percent	Plutonium, weight percent	Critical Radius, cm	Critical Mass, kg Pu
Plutonium Dioxide Density = 9 g/cc			
10	25.20	30.334	92.80
40	62.25	13.522	32.88
70	78.81	9.514	20.04
100	88.19	7.518	14.13
Plutonium Dioxide Density = 6 g/cc			
10	18.57	37.398	115.93
40	54.27	17.667	48.89
70	74.82	12.691	31.71
100	88.19	10.214	23.62
Plutonium Dioxide Density = 5 g/cc			
10	16.03	41.532	132.32
40	50.40	19.895	58.18
70	72.63	14.390	38.53
100	88.19	11.682	29.45

* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.

TABLE VI

CRITICAL RADII FOR INFINITE CYLINDERS
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM TETRAFLUORIDE AND ALUMINA*

Plutonium Tetrafluoride, volume percent	Plutonium, weight percent	Critical Radius, cm
Plutonium Tetrafluoride Density = 7 g/cc		
10	18.00	23.20
40	49.41	9.88
70	65.80	6.79
100	75.87	5.30
Plutonium Tetrafluoride Density = 5 g/cc		
10	13.80	27.69
40	43.36	12.48
70	62.48	8.65
100	75.87	6.83
Plutonium Tetrafluoride Density = 3 g/cc		
10	8.93	35.68
40	33.72	17.58
70	55.91	12.51
100	75.87	9.98

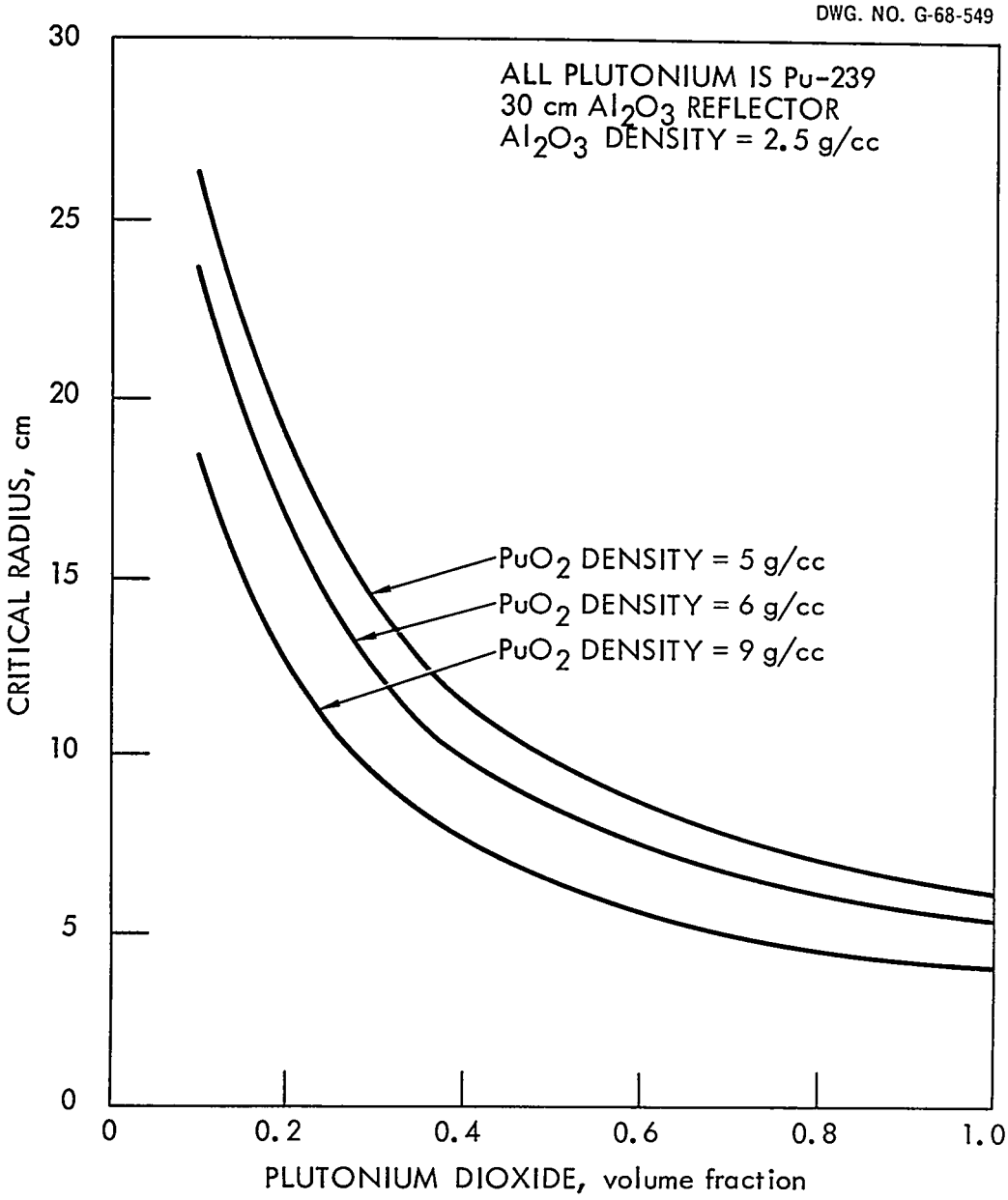
* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.

TABLE VII

CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM TETRAFLUORIDE AND ALUMINA*

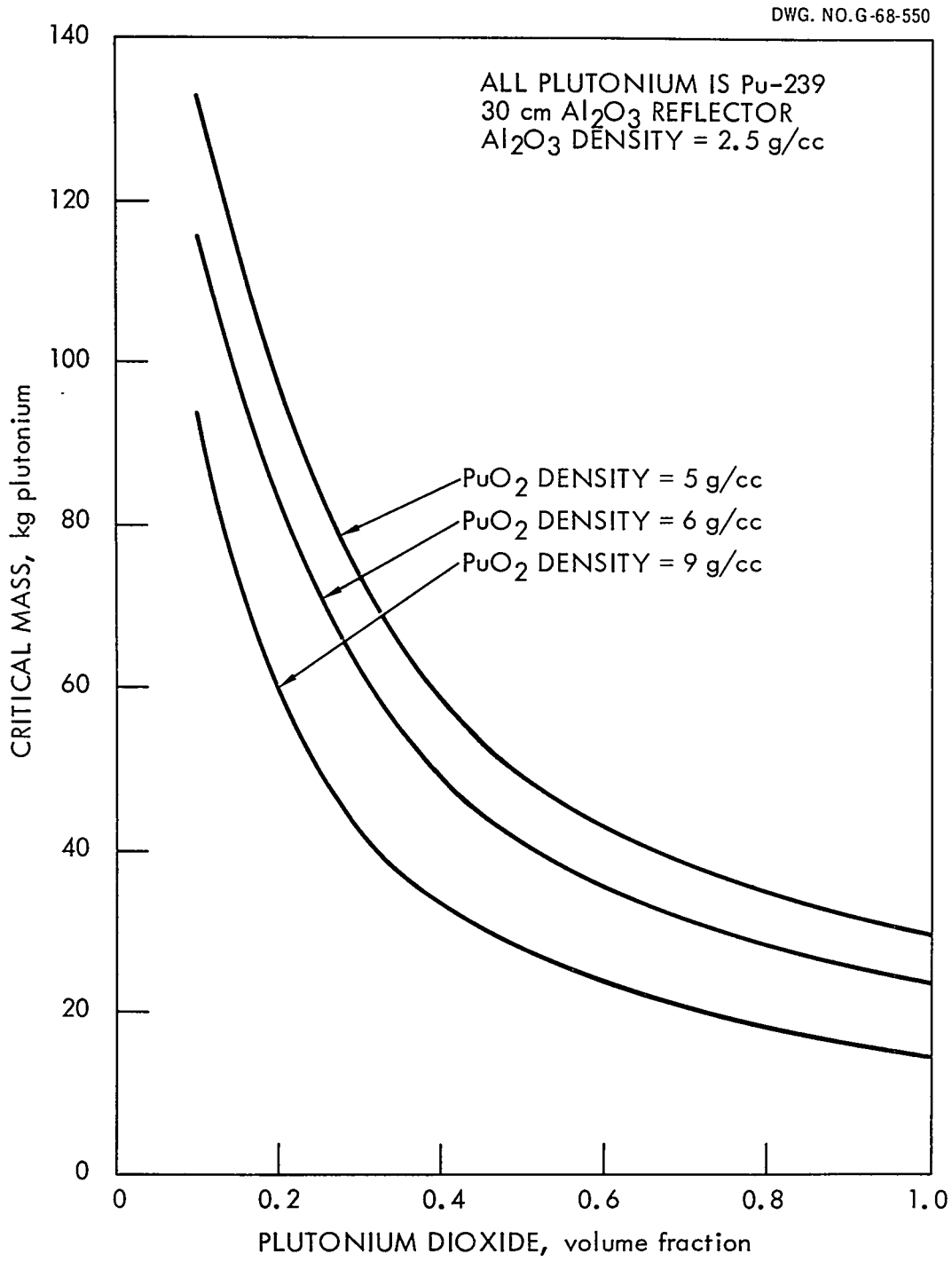
Plutonium Tetrafluoride, volume percent	Plutonium, weight percent	Critical Radius, cm	Critical Mass, kg Pu
Plutonium Tetrafluoride Density = 7 g/cc			
10	18.00	36.638	109.41
40	49.41	17.119	44.64
70	65.80	12.143	27.88
100	75.87	9.660	20.05
Plutonium Tetrafluoride Density = 5 g/cc			
10	13.80	43.942	134.83
40	43.36	21.318	61.58
70	62.48	15.392	40.56
100	75.87	12.454	30.70
Plutonium Tetrafluoride Density = 3 g/cc			
10	8.93	55.144	159.88
40	33.72	29.330	96.23
70	55.91	21.866	69.78
100	75.87	18.069	56.25

* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.



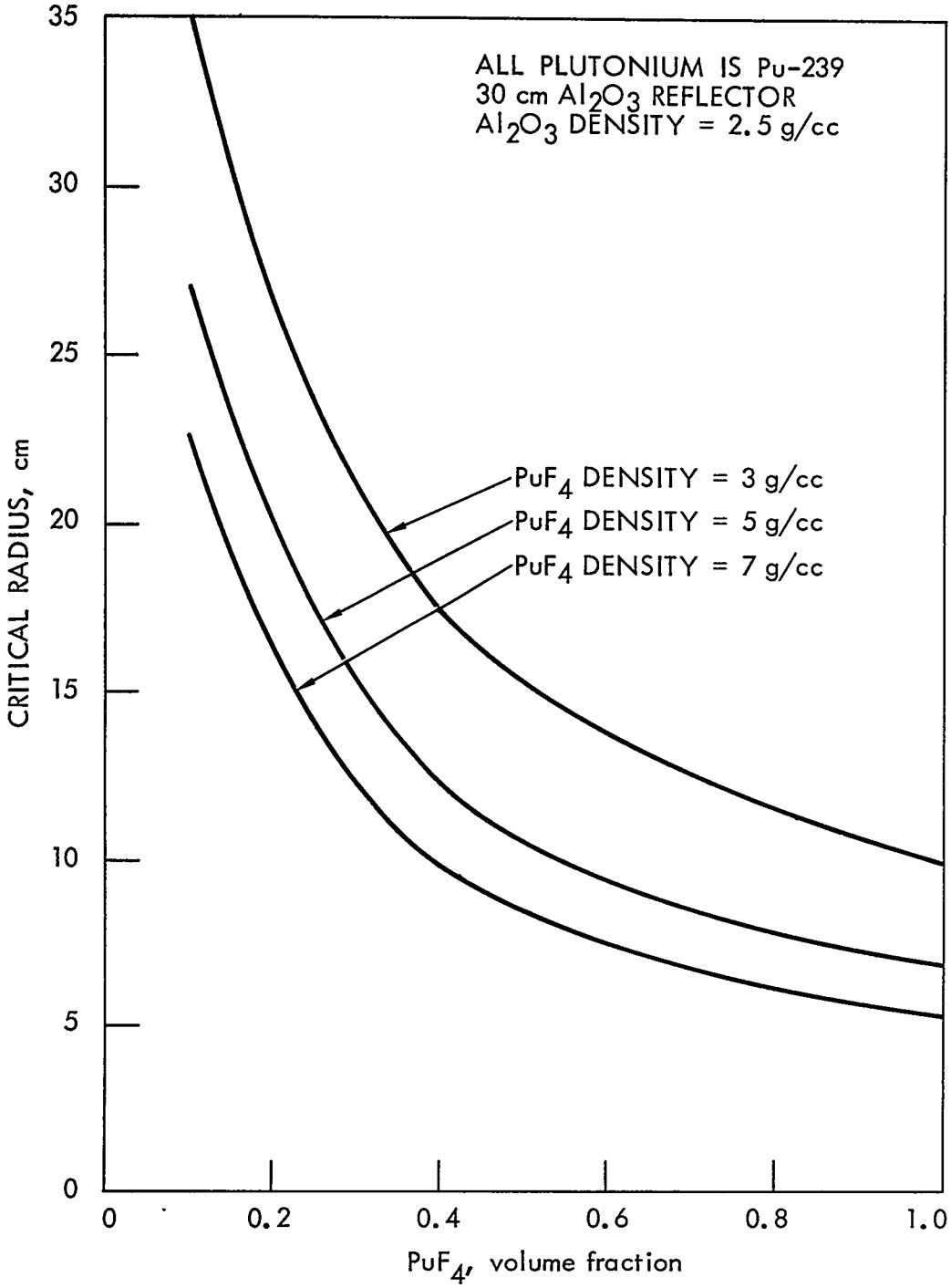
CRITICAL RADII FOR INFINITE CYLINDERS
CONTAINING HOMOGENEOUS MIXTURES OF
PLUTONIUM DIOXIDE AND ALUMINA

Figure 10



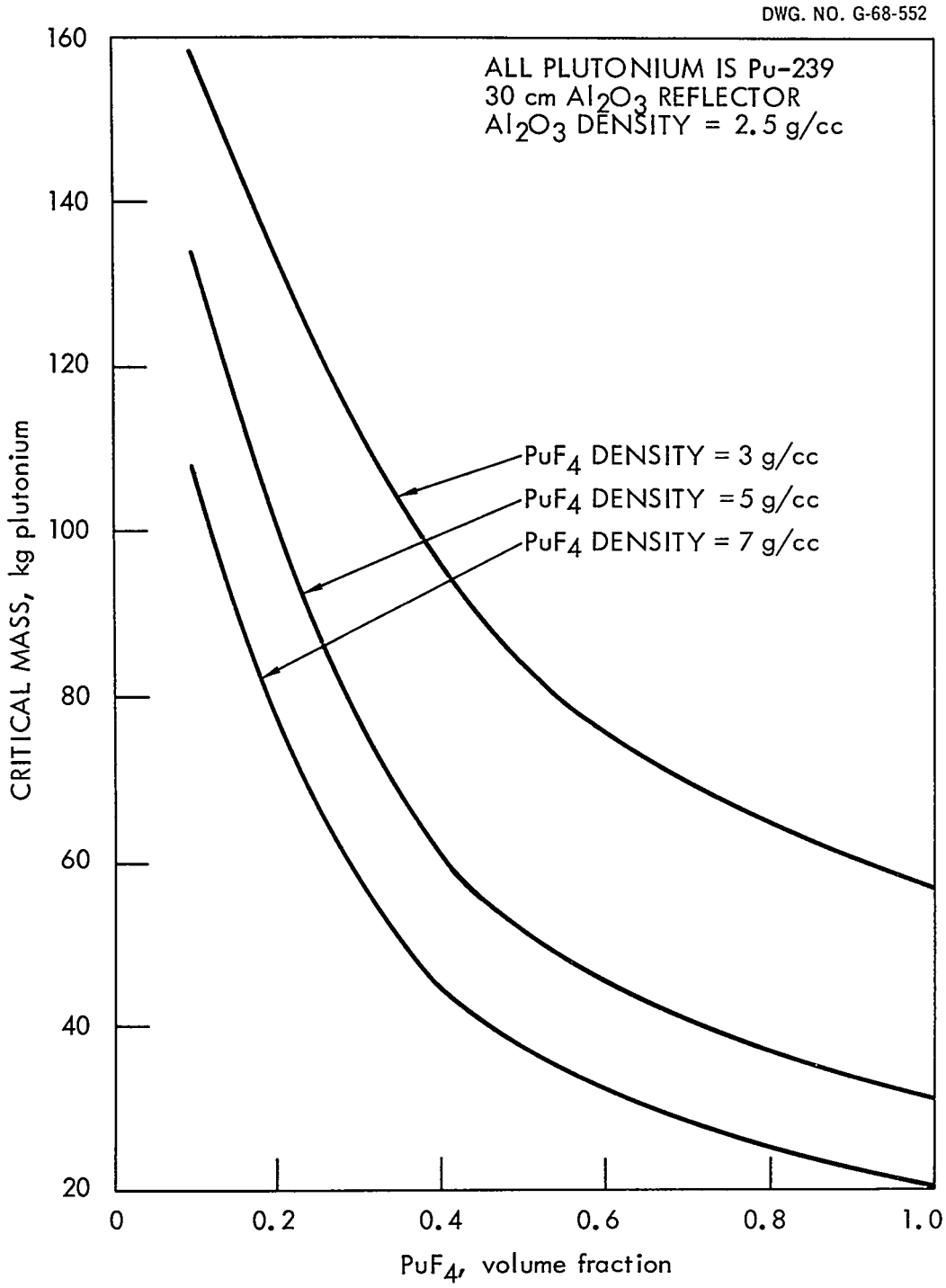
CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES OF
PLUTONIUM DIOXIDE AND ALUMINA

Figure 11



CRITICAL RADII FOR INFINITE CYLINDERS CONTAINING HOMOGENEOUS MIXTURES OF PuF_4 AND Al_2O_3

Figure 12



CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES OF
PuF_4 AND Al_2O_3

Figure 13

material and alumina were additive in the fuel mixtures. For example, consider the case for a basic plutonium dioxide density of 9 g/cc, with the plutonium present in a mixture having a composition of 40 volume percent plutonium dioxide and 60 volume percent alumina. For each 100 cc of fuel mixture, the volume occupied by the plutonium dioxide and by the alumina would be 40 and 60 cc, respectively. The weight of plutonium dioxide in the mixture would then be 40 × 9, or 360 grams, and thus, the resultant density of plutonium dioxide in the mixture would be 3.6 g/cc.

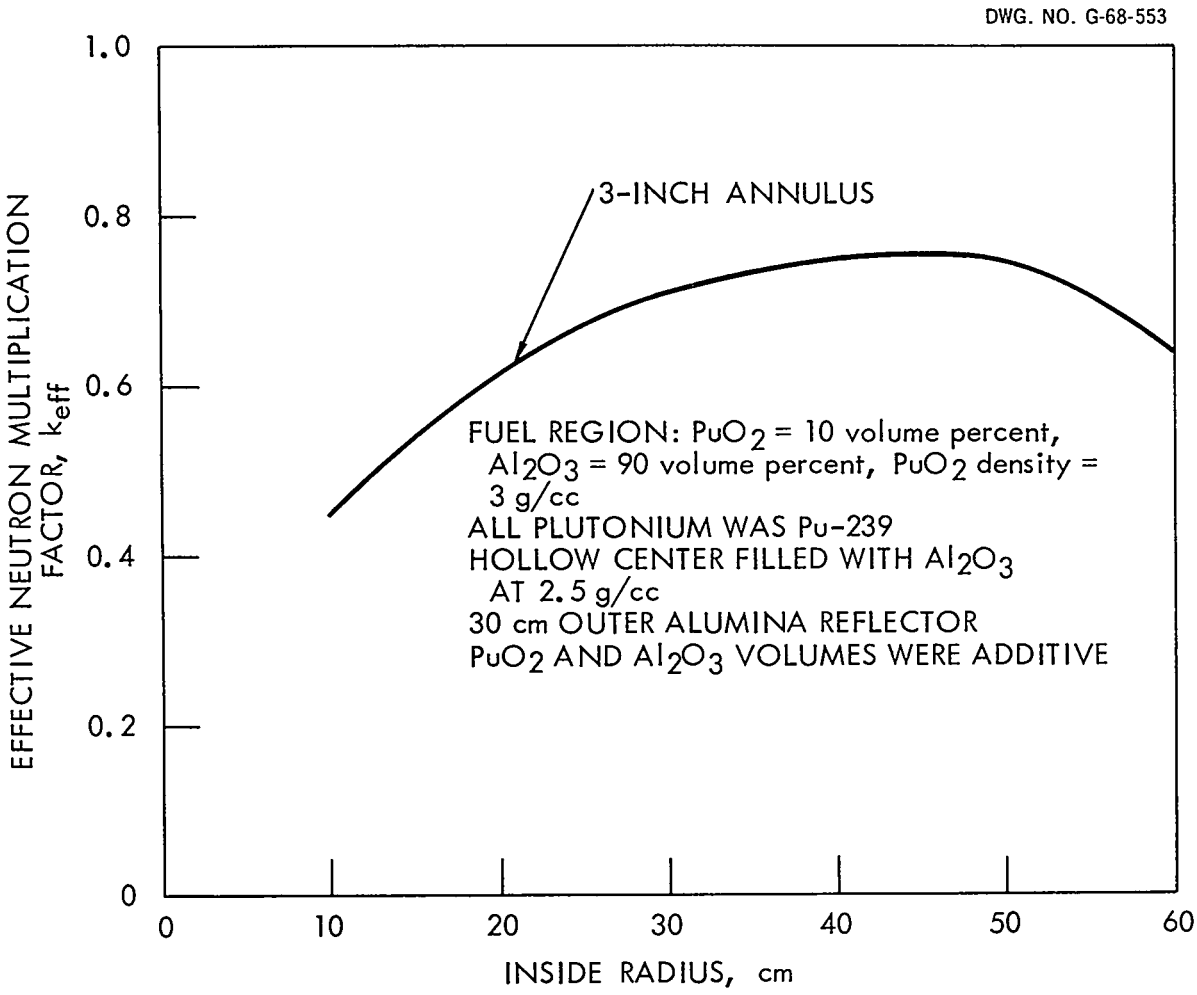
It can be seen from the results that the critical radii for infinite cylinders and the critical sphere masses are smaller for the high density (9 g/cc) plutonium dioxide cases than for the fully dense (7 g/cc) plutonium tetrafluoride cases.

Infinite Annuli. Calculations have also been made for homogeneous mixtures of plutonium dioxide and alumina contained in the annular space between two concentric cylinders. It was assumed for all cases that the inner cylinders were filled with alumina and that the outer cylinders were reflected with 30 cm of alumina. The alumina density was taken to be 2.5 g/cc, while the plutonium dioxide densities assumed were 3, 6, and 9 g/cc. All plutonium was considered to be plutonium-239. Annular thicknesses of 3, 4, 6, and 8 inches were investigated.

As the radius of an inner cylinder is increased while the annular thickness is kept constant, the effective neutron multiplication factor (k_{eff}) for the assembly first increases, then reaches a maximum, and finally decreases and approaches the value for an infinite slab (see figure 14).

The initial increase is due to the additional moderation as alumina is added to fill the expanding inner cylinder. As the inner radius is increased further, however, the system tends to uncouple, and the probability is reduced that neutrons emitted from one wall of the annulus in the direction of the center will reach the opposite annular wall. That is, as the spacing is increased, neutron interaction is reduced. Thus, at some point, the neutron multiplication factor begins to decrease.

A summary of calculated critical inner radii is presented in table VIII. In those cases in which it was not obvious that a critical radius existed, the ANISN transport code was used in the fixed radius option instead of the search option to avoid using excessive computer time. In the fixed radius option, the inner radius was specified along with the annular thickness and the fuel concentration, and the k_{eff} for the assembly was calculated. In subsequent calculations, the inner radius was progressively increased, and additional cases were run until a maximum k_{eff} was reached. Results for a typical subcritical assembly calculation are plotted in figure 14. The critical radius ($k_{eff} = 1.0$) was then found by interpolation; if the maximum k_{eff} was less than 1.0, it was, of course, concluded that the assembly would be subcritical for all inner radii. The critical radii determined in this manner, i.e., by interpolation, are denoted as approximate values in table VIII. For these cases, it is important to realize that only the first, or "smallest", critical radii



EFFECTIVE NEUTRON MULTIPLICATION FACTORS FOR INFINITE ANNULAR CYLINDERS OF HOMOGENEOUS MIXTURES OF PuO_2 AND ALUMINA

Figure 14

TABLE VIII

CALCULATED CRITICAL INNER RADII FOR ANNULAR CYLINDERS CONTAINING HOMOGENEOUS PLUTONIUM DIOXIDE AND ALUMINA MIXTURES*

Plutonium Dioxide, volume percent	First Critical Inside Radius, cm, for Given Annular Thickness			
	3 inches	4 inches	6 inches	8 inches
Plutonium Dioxide Density = 9 g/cc				
10	ca. 27.4	ca. 15.5	3.86	§
40	§	§	§	§
70	§	§	§	§
100	§	§	§	§
Plutonium Dioxide Density = 6 g/cc				
10	†	ca. 30.4	ca. 12.3	3.61
40	3.27	§	§	§
70	§	§	§	§
100	§	§	§	§
Plutonium Dioxide Density = 3 g/cc				
10	†	†	†	ca. 21.3
40	ca. 18.5	ca. 10	1.04	§
70	5.72	1.42	§	§
100	1.71	§	§	§

* The inner cylinder was filled with alumina and the outer cylinder was reflected with 30 cm of alumina. The alumina density was 2.5 g/cc. All plutonium was plutonium-239.

† Safe for all inner radii.

§ Supercritical for all inner radii.

are given. Since the k_{eff}'s reach maximum values and then decrease approaching the values for infinite slabs, it is obvious that for critical annulus cases where the k_{eff} for the infinite slab is less than 1.0, there will be a second radius, i.e., the "largest" critical radius, where the k_{eff}'s for the annular cylinders will again pass through 1.0. These values were not computed in this study, however, since most of the calculations were taken only to the point of locating the maximum k_{eff}. Additionally, for many of the cases summarized in table VIII, the assemblies were supercritical for all inner radii. These cases were those in which the annular thicknesses were larger than the radii of critical solid infinite cylinders of the same material, composition, and density.

Infinite Slabs. To aid in the annulus studies, criticality calculations were also made for infinite slabs containing mixtures of plutonium dioxide and alumina. The slabs were reflected on both sides with 30 cm of alumina. The fissile material densities assumed were the same as for the annular cases. In addition, the slab calculations were repeated for plutonium tetrafluoride at densities of 3, 5, and 7 g/cc. Results of these calculations are listed in tablex IX and X and are plotted in figures 15 and 16.

Finite Cylinders. Reactivity estimates, made using the KENO Monte Carlo code, have been made for finite, 10-inch-diameter cylinders of plutonium tetrafluoride at densities of 3, 5, and 7 g/cc. Several cases of reflection were assumed* for each calculation; these are explained and the computation results are detailed in tables XI through XIV for plutonium tetrafluoride at 5 and 7 g/cc. For plutonium tetrafluoride at 7 g/cc, a plutonium isotopic distribution other than pure plutonium-239 was also assumed for one calculation series.

As can be seen from the tables, the addition of a bottom alumina reflector increases the effective neutron multiplication factor for the smaller cylinder heights, but has a lesser effect on longer cylinders. This is because the longer cylinders are approaching the point where they are essentially infinite and do not "see" the alumina reflectors at the ends. The addition of nickel cladding has an appreciable effect on the k_{eff}'s for all cylinder heights. For the cases shown, the cladding increased the k_{eff}'s from 5 to 10%. Also, as might be expected, a reduction in the percentage of fissile plutonium causes a corresponding decrease in reactivity.

All of the cylinders containing plutonium tetrafluoride at 3 g/cc were well below critical. For the most reactive case at this density, i.e., reflected on top and bottom with alumina and clad with nickel, the k_{eff}

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* The basic approach was to begin with a bare cylinder and then add reflection in increments.

TABLE IX

CRITICAL THICKNESSES FOR INFINITE SLABS
CONTAINING HOMOGENEOUS PLUTONIUM DIOXIDE AND ALUMINA MIXTURES*

Plutonium Dioxide, volume percent	Plutonium, wt %	Critical Thickness, cm
Plutonium Dioxide Density = 9 g/cc		
10	25.20	11.37
40	62.25	3.12
70	78.81	1.80
100	88.19	1.26
Plutonium Dioxide Density = 6 g/cc		
10	18.57	16.06
40	54.27	4.65
70	74.82	2.70
100	88.19	1.89
Plutonium Dioxide Density = 3 g/cc		
10	10.38	26.92
40	39.20	9.07
70	64.98	5.37
100	88.19	3.79

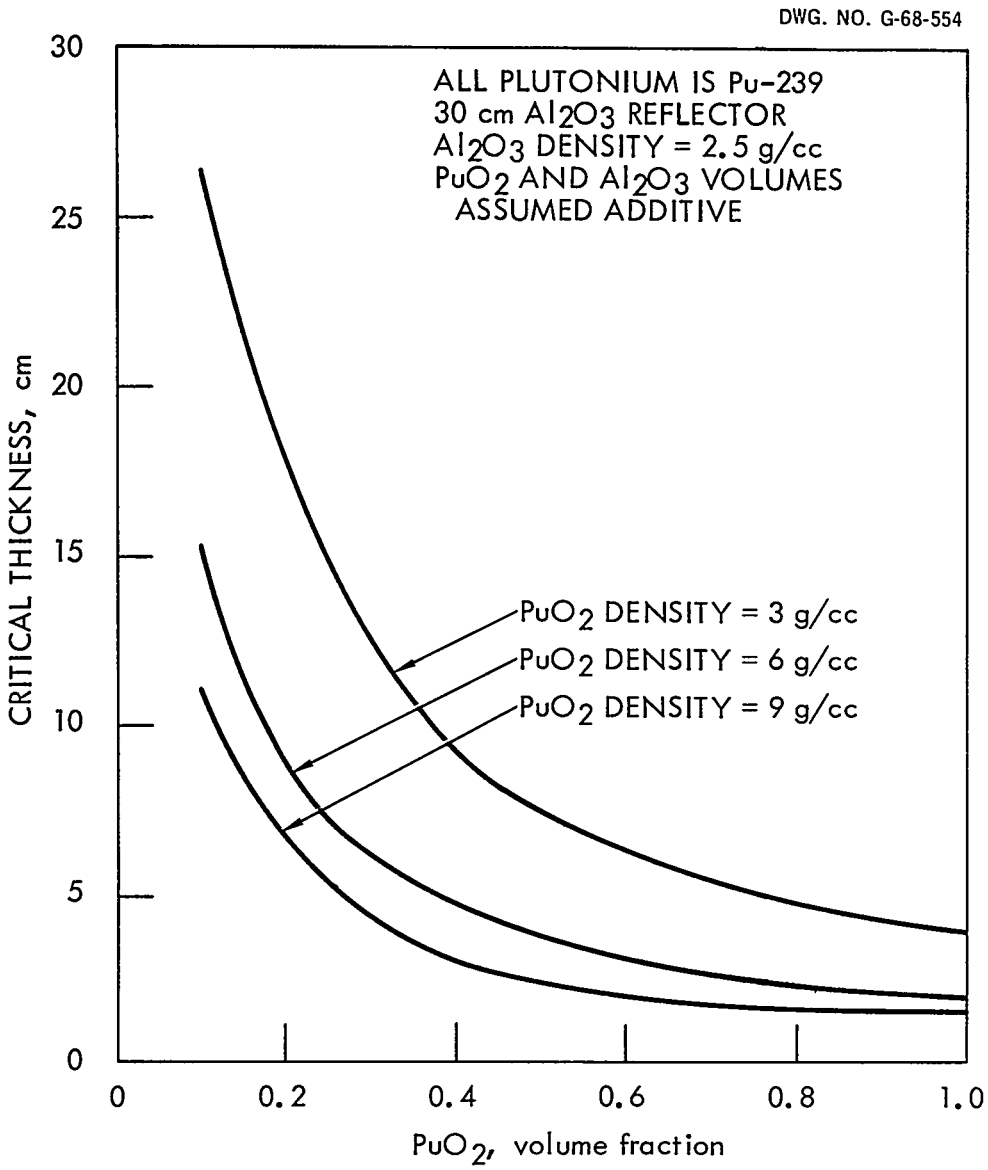
* Slabs reflected on both sides by 30 cm of alumina at a density of 2.5 g/cc. All plutonium was plutonium-239.

TABLE X

CRITICAL THICKNESSES FOR INFINITE SLABS
CONTAINING HOMOGENEOUS PLUTONIUM TETRAFLUORIDE AND ALUMINA MIXTURES*

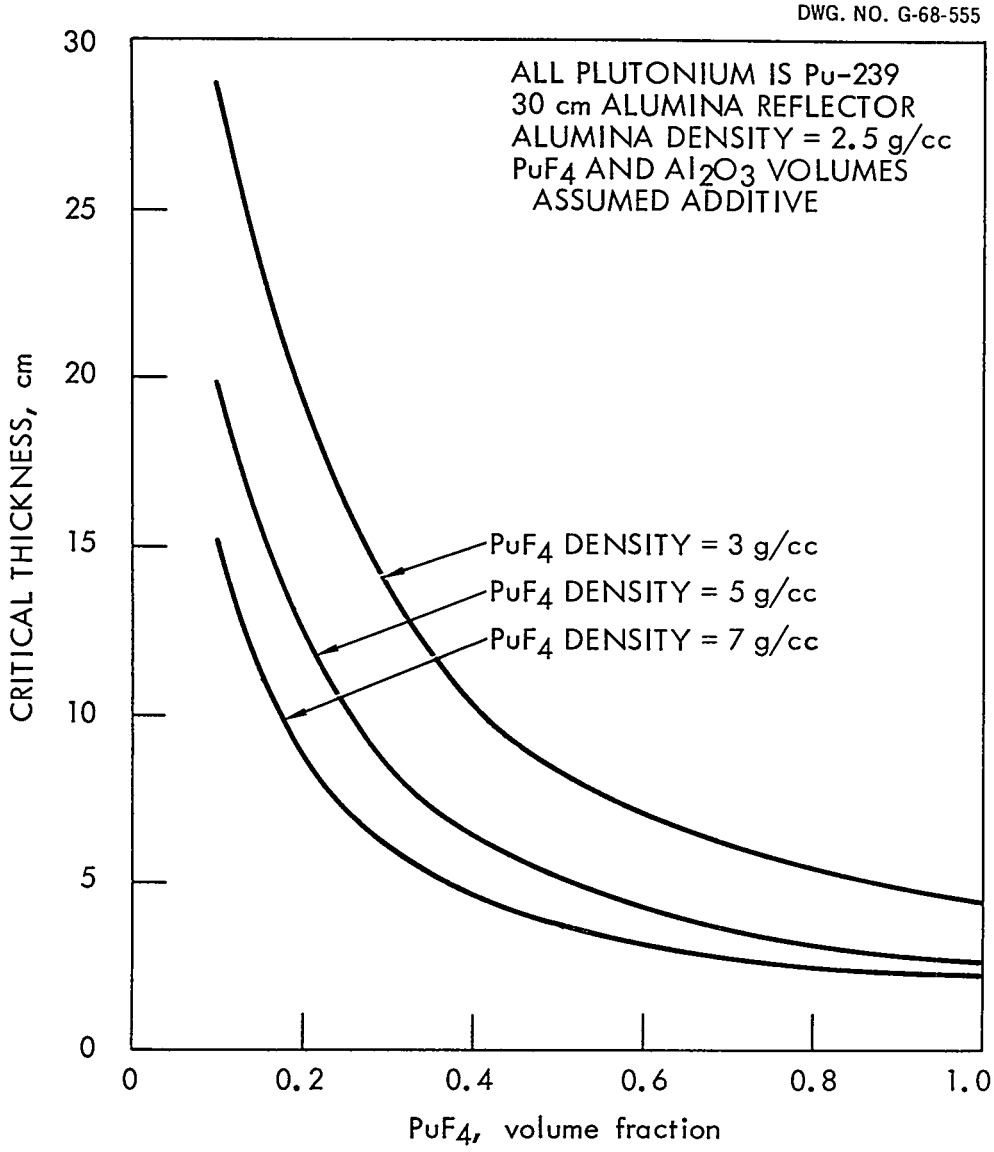
Plutonium Tetrafluoride, volume percent	Plutonium, wt %	Critical Thickness, cm
Plutonium Tetrafluoride Density = 7 g/cc		
10	18.00	15.73
40	49.41	4.59
70	65.80	2.67
100	75.87	1.88
Plutonium Tetrafluoride Density = 5 g/cc		
10	13.80	20.35
40	43.36	6.36
70	62.48	3.72
100	75.87	2.63
Plutonium Tetrafluoride Density = 3 g/cc		
10	8.93	29.30
40	33.72	10.32
70	55.91	6.16
100	75.87	4.38

* Slabs reflected on both sides by 30 cm of alumina at a density of 2.5 g/cc. All plutonium was plutonium-239.



CRITICAL THICKNESSES FOR INFINITE SLABS CONTAINING HOMOGENEOUS MIXTURES OF PuO_2 AND ALUMINA

Figure 15



CRITICAL THICKNESSES FOR INFINITE SLABS CONTAINING HOMOGENEOUS MIXTURES OF PuF_4 AND ALUMINA

Figure 16

TABLE XI

INPUT PARAMETERS FOR CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 5 g/cc

Parameters	Case I	Case II	Case III
Top Reflector	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3
Bottom Reflector	none	100 cm Al_2O_3	100 cm Al_2O_3
Wall Cladding	none	none	1.27 cm Ni
Isotopic Distribution	100% Pu-239	100% Pu-239	100% Pu-239

TABLE XII

RESULTS OF CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 5 g/cc

Cylinder Height, cm	Plutonium, kg	Effective Neutron Multiplication Factors		
		Case I	Case II	Case III
10	19.2		0.579 ± 0.003	0.634 ± 0.004
12	23.1		0.621 ± 0.003	0.669 ± 0.004
15	28.8		0.687 ± 0.004	0.738 ± 0.004
20	38.4		0.736 ± 0.004	0.802 ± 0.005
25	48.0	0.755 ± 0.004	0.774 ± 0.004	0.837 ± 0.004
35	67.3	0.812 ± 0.004	0.827 ± 0.004	0.905 ± 0.004
50	96.1	0.858 ± 0.004	0.874 ± 0.004	0.952 ± 0.004
100	192.2	0.919 ± 0.004	0.913 ± 0.005	1.000 ± 0.004
200	384.5		0.938 ± 0.004	

* Based on parameters in table XI.

TABLE XIII

INPUT PARAMETERS FOR CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc

Parameter	Numerical Value			
	Case I	Case II	Case III	Case IV
Top Reflector	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3
Bottom Reflector	none	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3
Wall Cladding	none	none	1.27 cm Ni	none
Isotopic Distribution	100% Pu-239	100% Pu-239	100% Pu-239	56% Pu-239 34% Pu-240 7% Pu-241 3% Pu-242

TABLE XIV

RESULTS OF CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc*

Cylinder Height, cm	Plutonium, kg	Effective Neutron Multiplication Facotrs			
		Case I	Case II	Case III	Case IV
8	21.5		0.738 ± 0.004	0.776 ± 0.005	
10	26.9	0.741 ± 0.004	0.809 ± 0.004	0.859 ± 0.005	
12	32.3	0.818 ± 0.004	0.872 ± 0.005	0.930 ± 0.005	0.776 ± 0.004
15	40.4	0.897 ± 0.004	0.947 ± 0.005	1.004 ± 0.005	0.833 ± 0.004
20	53.8	0.985 ± 0.005	1.028 ± 0.005	1.087 ± 0.005	0.916 ± 0.004
25	67.3	1.065 ± 0.005			0.967 ± 0.004
100	269.1				1.117 ± 0.005

* Based on parameters in table XIII.

was 0.637 ± 0.004* at a cylinder height of 200 cm. It was concluded that 10-inch-diameter cylinders of plutonium tetrafluoride at a density of 3 g/cc would be subcritical for all heights under the reflection conditions assumed.

Finite Slabs. Monte Carlo calculations were also made for finite slabs, 4 inches thick by 2 feet long. Plutonium tetrafluoride densities of 3, 5, and 7 g/cc were again investigated with the same conditions of reflection as were assumed for the cylinder cases. The nickel cladding was assumed to be located on the faces of the slabs but not on the edges. The results for the 7 g/cc case are shown in tables XV and XVI.

All of the slabs of plutonium tetrafluoride at densities of 3 and 5 g/cc were found to be below critical. For the most reactive of these lower density cases, i.e., plutonium tetrafluoride at 5 g/cc, reflected on top and bottom with alumina and clad on the sides with nickel, the computed k_{eff} was 0.779 ± 0.004 at a slab height of 100 cm. It was concluded that 4-inch-thick by 2-foot-long slabs of plutonium tetrafluoride at 3 and 5 g/cc densities would be subcritical for all heights under the reflection conditions assumed.

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* The k_{eff} value obtained by the Monte Carlo procedure represents an average of k_{eff} numbers computed for many different neutron batches. The qualification placed on this average (± 0.004 in this case) is one standard deviation based on the mathematics of the calculation. It is reported only to show the spread of the individually computed k's and is not an indication of the absolute accuracy of the results.

TABLE XV

INPUT PARAMETERS FOR CRITICALITY CALCULATIONS
FOR FINITE 4-INCH-THICK BY 2-FOOT-LONG SLABS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc

Parameter	Numerical Value			
	Case I	Case II	Case III	Case IV
Top Reflector	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3
Bottom Reflector	none	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3
Wall Cladding	none	none	1.27 cm Ni*	none
Isotopic Distribution	100% Pu-239	100% Pu-239	100% Pu-239	56% Pu-239 34% Pu-240 7% Pu-241 3% Pu-242

* The cladding was on only the two large faces of the slabs and extended to the levels of the top and bottom alumina reflectors.

TABLE XVI

RESULTS OF CRITICALITY CALCULATIONS
FOR FINITE 4-INCH-THICK BY 2-FOOT-LONG SLABS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc*

Slab Height, cm	Plutonium, kg	Effective Neutron Multiplication Factors			
		Case I	Case II	Case III	Case IV
12	39.5			0.744 ± 0.004	
15	49.3		0.714 ± 0.004	0.801 ± 0.004	
20	65.8	0.749 ± 0.004	0.776 ± 0.003	0.866 ± 0.004	
30	98.7	0.817 ± 0.004	0.822 ± 0.004	0.935 ± 0.004	
50	164.5	0.863 ± 0.004	0.857 ± 0.005	0.997 ± 0.004	
100	329.0	0.892 ± 0.005	0.895 ± 0.004		0.799 ± 0.004

* Based on parameters in table XV.

PROTOTYPE TESTING AND EVALUATION

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T. H. Monk, M. J. Stephenson

Activities were conducted according to the guidelines in the close-out plan for the Oak Ridge Gaseous Diffusion Plant fluoride volatility program. The work covered the zircaloy decladding, uranium dioxide oxidation, and fluorination phases of the process. Projects included runs in the semiworks facility, filter multiple exposure tests, a continuation of the long-term testing of the peripheral compressor, and product purification by sorption on sodium fluoride.

Formal topical reports will be issued shortly detailing the results of the major experimental work conducted during this program. The subjects which have been covered separately include semiworks plant tests, filter exposure tests, peripheral compressor work, and the bromine pentafluoride spill experiments which were conducted last year. In addition, a movie showing bromine pentafluoride spill tests in progress was prepared.

PROCESS AND REACTOR STUDIES

Additional semiworks tests were conducted under this phase of the program. The work encompassed the effect of various parameters on elutriation; the feasibility of semicontinuous pellet feeding during oxidation; fuel element decladding, followed by conversion of the released uranium to U_3O_8; and the use of 40% oxygen instead of lower oxygen concentrations in the oxidation step.

Semiworks Plant Tests

Twelve runs (UE-43 through -54) were conducted during this report period. In all the runs, 1/4- to 1/2-inch-diameter Alcoa T-164 alumina balls were added to position the uranium charge in the 10-inch-diameter section of the reactor about 1 foot above the top of the transition piece, while Alcoa T-61 tabular alumina powder, nominally minus 48- plus 100-mesh, was used in the reactor as bed diluent and in the filter cooler as a cooling bed. In all runs, 1/4- to 1/2-inch-diameter alumina balls were added to the reactor first, the uranium charge next, and the alumina powder last. Charges from various sources were involved in the testing, including annular EGCR or solid cylindrical Westinghouse pellets*, a PRTR fuel element containing vibratory compacted uranium dioxide, and an ORGDP-fabricated simulated fuel element containing solid cylindrical pellets.

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* Obtained from scrap aluminum-clad fuel rods supplied by Bettis Atomic Laboratories. The normal assay, 1/2-inch-diameter by 3/4-inch-long pellets, were removed by physically peeling off the soft cladding. The rods had been utilized in a zero power critical facility operation.

Runs UE-43, -44, and -46, were made to study the effects of hydrogen chloride pretreatment of EGCR uranium dioxide fuel pellets, length of exposure to hydrogen chloride, and superficial velocity on U_3O_8 elutriation during the oxidation step. Run UE-43 was an oxidation run at the usual system backpressure and a superficial gas velocity of 2.4 ft/sec, which is the highest undertaken in tests in this program. With regard to operating steps, velocities, and reactant gas concentrations, UE-44 was similar to run UE-40, reported previously, in which the effect on U_3O_8 elutriation brought about by hydrogen chloride contacting a uranium dioxide pellet charge in the absence of zirconium was studied*. The hydrogen chloride treatment before oxidation lasted 4 hours in each case. The two runs differed only in that normal oxidation pressures were used in UE-44 while higher values were employed in UE-40. In UE-46, the time for the hydrogen chloride cycle was reduced to 1 hour to see if length of hydrogen chloride exposure is a major factor affecting elutriation.

Runs UE-45 and -48 were batch type tests with normal assay Westinghouse uranium dioxide fuel pellets. They were undertaken to see if the material from this new source could be processed without major difficulties. Because of the assay, this type of pellet could be tested in semiworks equipment without criticality limitations on the amount of uranium fed or accumulated; the material was ideally suited for use in planned semicontinuous feeding experiments with large charges. Operating conditions were chosen for run UE-45 to determine if good oxidation to U_3O_8 could be achieved in only 2 hours with air from the outset; and, for elutriation purposes, nitrogen was used for an additional 6 hours after cessation of air flow. Run UE-48 was conducted with the oxidation reaction time extended from 2 to 8 hours.

In UE-47, decladding and oxidation were carried out with a "cold" normal assay PRTR fuel element. This test was the first in the semiworks plant with an actual reactor fuel assembly. The PRTR fuel assembly was about 8 feet long and contained eighteen zircaloy-clad fuel rods. Each rod, which contained ceramic vibratory compacted uranium dioxide, was wrapped with wire to maintain spacing over the full length. The two end brackets were made of stainless steel, while the tubing, wire wrap, and end caps were zircaloy-2. The element originally had nineteen tubes in the cluster; however, the center rod was replaced with a thermowell so that, during the run, reaction temperatures at various positions along the longitudinal axis could be followed.

Runs UE-49, -50, and -52 featured semicontinuous pellet feeding during oxidation. This mode of feeding could be employed in a plant in which spent fuel rods would be declad mechanically with the pellets collected for salvage processing. In these runs, the pellets were fed to the

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* Pashley, J. H., Schappel, R. B., ORGDP Fuel Reprocessing Studies, Summary Progress Report, July through December, 1967, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, July 17, 1968 (K-1744), pp. 46-47.

reactor through a hold volume attached to the charging port at the top of the reactor. This pellet charger is shown in figure 17 and consists of a 2-inch-diameter pipe, 2 feet 6 inches long, with ball valves on either end. Both valves were kept shut during the usual oxidation operation. When a batch of pellets was charged, the top valve was opened, pellets were loaded into the pipe, and the top valve was then closed. The lower valve was opened to allow the pellets to fall out of the pipe and into the reactor. In each run, an initial charge of pellets was placed directly in the reactor before startup so that an oxidation environment could be established before semicontinuous feeding commenced. EGCR pellets were used in UE-49, while Westinghouse pellets were fed to the reactor in both UE-50 and -52. Air was used as the oxidizing reagent in UE-49, but 40% oxygen was used in the two later runs.

Semicontinuous feeding of alumina to the filter cooler and removal of fluid-bed powder from the cooler were also attempted during oxidation in UE-50. A hold volume was mounted on the alumina fill port at the side of the filter cooler for the charging, while another volume for the collection of dumped powder was installed on the bottom valve. The overflow line on the filter cooler was shut off with a pipe cap before the run so that powder would leave the vessel only through the dump valve.

Runs UE-51 and -53 were made to study the oxidation reaction when 40% oxygen is used. The concentration was achieved by mixing air and oxygen at a 3.1 to 1.0 volume (flow) ratio. Westinghouse pellets were used in the first run and EGCR pellets in the second under identical operating conditions to highlight differences in material response to treatment.

In the final test, UE-54, the second of the two simulated fuel elements fabricated in the ORGDP shops* was processed through the decladding and oxidation steps. The dimensions of the element were the same as those reported for the first test†. Hydrogen chloride was used to volatilize the zircaloy cladding from the element, and the freed uranium dioxide pellets were oxidized with 40% oxygen.

The same six filter tubes were in use throughout this report period. Actually, these tubes had been used in most of the semiworks tests since the start of the program. Their permeabilities have been occasionally re-established by backflushing with water. After UE-49, the filters were inspected and found to be about 50% coated with a 1/16-inch-thick layer of gray powder. The filters were washed with water and reinstalled in the filter cooler for the remainder of the tests.

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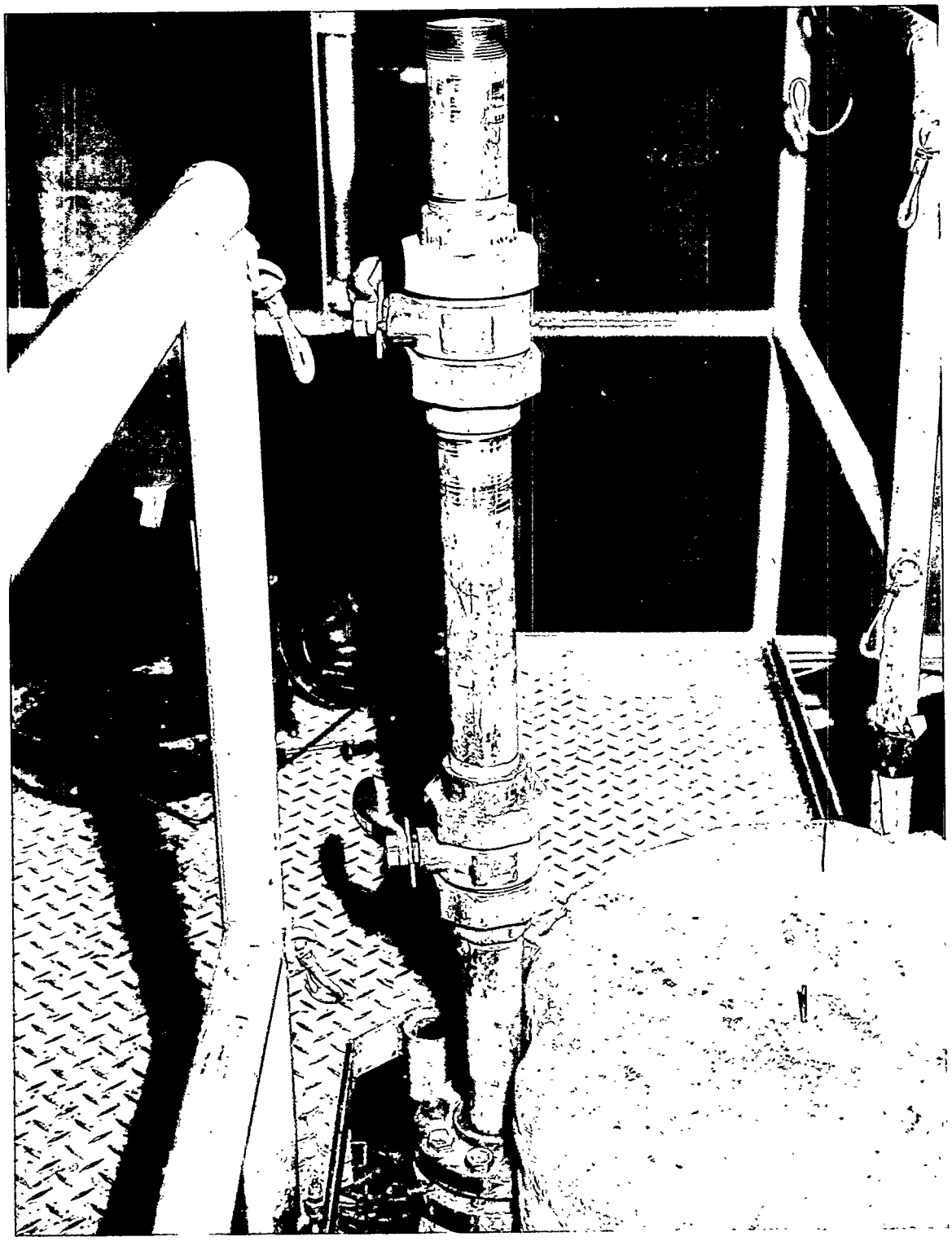
* Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies, Summary Progress Report, January through June, 1967, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, May 9, 1968 (K-1738), p. 56.

† K-1744, loc cit, p. 37.

PHOTO NO. PH-68-200



PELLET CHARGER

Figure 17

Pertinent information on run conditions, including charge weights, operating conditions, and reagent concentrations, is contained in table XVII. Run results are summarized in table XVIII. Run commentary details are as follows:

Run UE-43. The restriction placed in the vent line for runs UE-39 through -42 to achieve higher-than-normal system backpressures was removed after the completion of run UE-42. After the system was charged for UE-43, heatup was begun with the bed of alumina powder in the reactor fluidized with nitrogen at a velocity of 0.5 ft/sec in the 10-inch-diameter section. When the system temperatures stabilized, the inlet flows were adjusted to give 11% oxygen and a velocity of 2.5 ft/sec in the 10-inch-diameter section of the reactor at operating conditions, i.e., 490°C and 2 psig. These conditions were maintained for 2 hours; all flows were then shut off, and the filter cooler and receiver were emptied. The recovered material (U_3O_8 and alumina) was weighed and sampled for analysis. System temperatures remained constant even though there was no flow through the system.

The filter cooler was recharged with 11.4 kg of fresh minus 48- plus 100-mesh alumina powder and oxidation was resumed using 21% oxygen and a velocity of 2.4 ft/sec in the 10-inch-diameter part of the reactor at operating conditions. After an additional 3 hours of oxidation, the filter cooler and receiver were again emptied, and the filter cooler was recharged as before. Operation was then resumed for the last 3 hours of oxidation with 21% oxygen and a velocity of 2.4 ft/sec at 460°C and 4.0 psig in the 10-inch-diameter section of the reactor. Again, at the end of the test, the material in the filter cooler and receiver was weighed and sampled.

No operational problems were encountered during the total 8 hours of the oxidation step. During this time, 97.5% of the pellet charge was oxidized and 73.5% of the uranium was elutriated to the filter cooler. The cumulative weights of U_3O_8 and alumina elutriated as a function of oxidation time are plotted in figure 18. Screen analysis indicated that 95.9% of the uranium charge was comminuted to minus 35-mesh material.

Run UE-44. As noted above, this run was made to provide additional data on the effect on elutriation during oxidation resulting from prior exposure of the pellets to hydrogen chloride in the absence of cladding material, i.e., zirconium. Hydrogen chloride flow was started after the temperatures in the fluid bed were established at 390°C during heatup. Flows were adjusted to give a 30% hydrogen chloride-70% nitrogen gas feed and a superficial gas velocity of 0.6 ft/sec in the 10-inch-diameter section based on operating conditions of 390°C and 0.9 psig. The scrubber water flow rate was maintained at approximately 1.9 gpm, and the hydrogen chloride analysis averaged about 1.52 weight percent. The hydrogen chloride step was discontinued after 4 hours, and the system was purged for 1 hour with nitrogen at a velocity of 0.5 ft/sec in the 10-inch-diameter section of the reactor while the pellet bed was heated to 480°C. After the system had been purged, all flows were shut off, and the filter cooler was emptied. About 10.4 kg of alumina powder was recovered. The overflow

TABLE XVII

SUMMARY OF SEMIWORKS RUN CONDITIONS

	Run Number											
	UE-43	UE-44	UE-45	UE-46	UE-47	UE-48	UE-49	UE-50	UE-51	UE-52	UE-53	UE-54
Reactor Charge												
Support for Fluid Bed:												
1/4- to 1/2-Inch Alumina Balls, kg	79.5	79.5	79.5	79.5	79.5	80.0	79.5	79.5	79.5	79.5	79.5	79.5
Bed Diluent:												
Alumina Powder (minus 48 plus 100 mesh), kg	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	45.4
Uranium Dioxide Pellets, kg	64.9	64.9	64.9	64.9	46.6	64.9	63.6*	201.1†	65.0	201.1†	65.0	52.7
Type of Pellet or Element‡	a	a	b	a	c§	b	a	b	b	b	a	d
Pellet Charge Method**	a	a	a	a	a	a	b	b	a	b	a	a
Zircaloy, kg	0	0	0	0	11.1	0	0	0	0	0	0	23.2
Charge Weight Ratio, diluent powder-to-uranium	1.0	1.0	1.0	1.0	1.4	1.0	*	†	1.0	†	1.0	1.0
Initial Filter Cooler Charge												
Alumina Powder (minus 48 plus 100 mesh), kg	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4
Declad Cycle												
Feed Gas Concentration in Nitrogen:												
Hydrogen Chloride, vol %		30		29	25 30 22 40 40							20 35 60
Hydrogen, vol %		0		0	0 0 0 0 0							0 0 0
Operating Time, hr		4		1	0.5 2.75 0.5 0.3 3.3							4 4 6
Operating Temperature, °C		390		410	410 410 410 410 410							425 370 370
Inlet Gas Temperature, °C		330		370	340 340 350 340 350							370 370 370
Filter Temperature, °C					310							315
Approximate Superficial Velocity in 10-Inch-Diameter Section, ft/sec		0.6		0.6	0.9 0.9 0.8 1.0 0.5							0.7 0.7 0.6
Oxidation Cycle												
Oxygen Concentration in Nitrogen, vol %	11 21 21	11 21	21 0†† 0††	10 21 21	21 21 21	21 21 21	21	21	40	40	40	40
Operating Time, hr	2 3 3	2 2	2 3 3	2 3 3	2 3 3	2 3 3	9	15.5	3	10	3	4
Reaction Oxidation Temperature, °C	490 460 460	480 480	450 440 440	500 490 490	460 445 450	470 470 470	450	465	480	454	500	500
Approximate Superficial Velocity in 10-Inch-Diameter Section, ft/sec	2.5 2.4 2.4	1.8 1.4	2.3 2.2 2.1	1.7 1.4 1.5	1.3 1.3 1.3	1.8 1.8 2.0	1.7	1.6	1.6	1.5	1.7	1.5
Reaction Pressure Above Fluid Bed, psig	2.0 4.8 4.0	0.8 2.9	3.2 1.8 1.7	1.3 1.4 0.6	1.4 0.9 0.8	3.4 3.4 2.2	4.6	5.8	2.0	2.4	1.1	4.0

* Only 31.8 kg of uranium dioxide was charged initially; thus, the initial diluent alumina-to-uranium ratio was 1.8. During oxidation, an additional 31.8 kg of uranium dioxide was added. A later alumina powder-to-uranium ratio, based on the full 63.6 kg charge, would be 1.0.

† Only 64.9 kg of uranium dioxide was charged initially to the reactor; the initial diluent alumina-to-uranium ratio was 1.0. During oxidation, an additional 136.2 kg of uranium dioxide was added. A later alumina powder-to-uranium ratio, based on the full 201.1 kg charge, would be 0.3.

‡ Pellet types are designated as follows: a - EGCR; b - Westinghouse solid cylinder; c - PRTR element; d - solid cylinders in simulated elements.

§ The charge for this run was a PRTR fuel element containing vibratory compacted uranium dioxide.

** The pellet charge method is coded as: a - batch; b - semicontinuous.

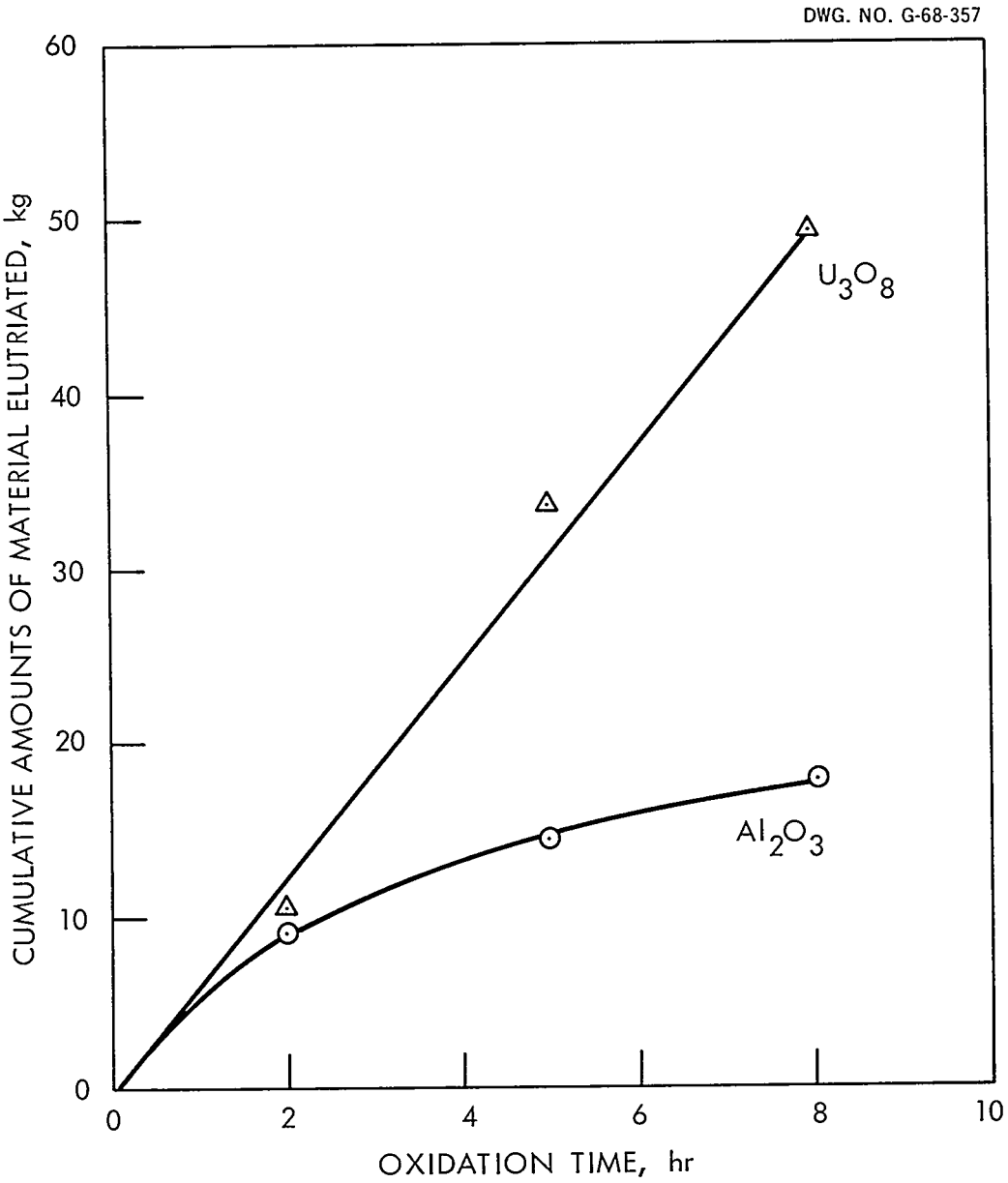
†† Nitrogen flow only was used during these periods.

TABLE XVIII

SUMMARY OF SEMIWORKS RUN RESULTS

	Run Number											
	UE-43	UE-44	UE-45	UE-46	UE-47	UE-48	UE-49	UE-50	UE-51	UE-52	UE-53	UE-54
Material Balances ($\frac{\text{weight recovered} \times 100}{\text{weight charge}}$), %												
Gross Weight Basis	99.9	98.4	100.1	100.3	100.4	99.8	100.3	95.9	107.2	99.2	100.0	95.0
Uranium Basis	99.5	93.3	103.0	102.8	97.3	105.0	103.8	98.0	104.2	98.9	103.3	98.3
Declad Cycle												
Zirconium Remaining in Bed, percent of original charge		*		*	16.2							7.4
Oxidation Cycle												
Pellet Charge Oxidized to U_3O_8, %	97.5	97.1	98.2	96.0	93.5	98.3	97.8	99.2	95.9	99.5	99.1	97.1
Pellet Charge Comminuted to minus 35 mesh, %	95.9	95.6	76.7	98.3	100.0	88.7	98.5	71.4	55.2	75.1	95.5	99.4
Charge Elutriated from Reactor During Oxidation, %												
Diluent Powder plus Uranium Dioxide Pellets	55.4	40.3	42.9	58.1	48.1	60.6	38.2	28.0	36.0	34.1	28.2	62.0
Uranium	73.5	62.1	54.5	98.3	90.3	88.7	63.9	25.7	33.7	29.3	44.8	88.6
Diluent Powder	31.3	12.5	27.1	7.7	10.5	24.5	6.5	32.5	37.1	46.9	7.2	21.6
U_3O_8 Equivalent in Material Elutriated, weight percent	73.5	85.5	70.5	93.8	88.0	81.1	92.1	74.4	52.0	69.7	88.2	79.8
Elutriation Rate, kg U/hr of run time	5.2	7.1	3.9	7	4.6	6.3	4	2.9	6.4	5.1	8.5	10.3

* No zirconium charge to bed.



U_3O_8 AND ALUMINA ELUTRIATION DURING OXIDATION IN UE-43

Figure 18

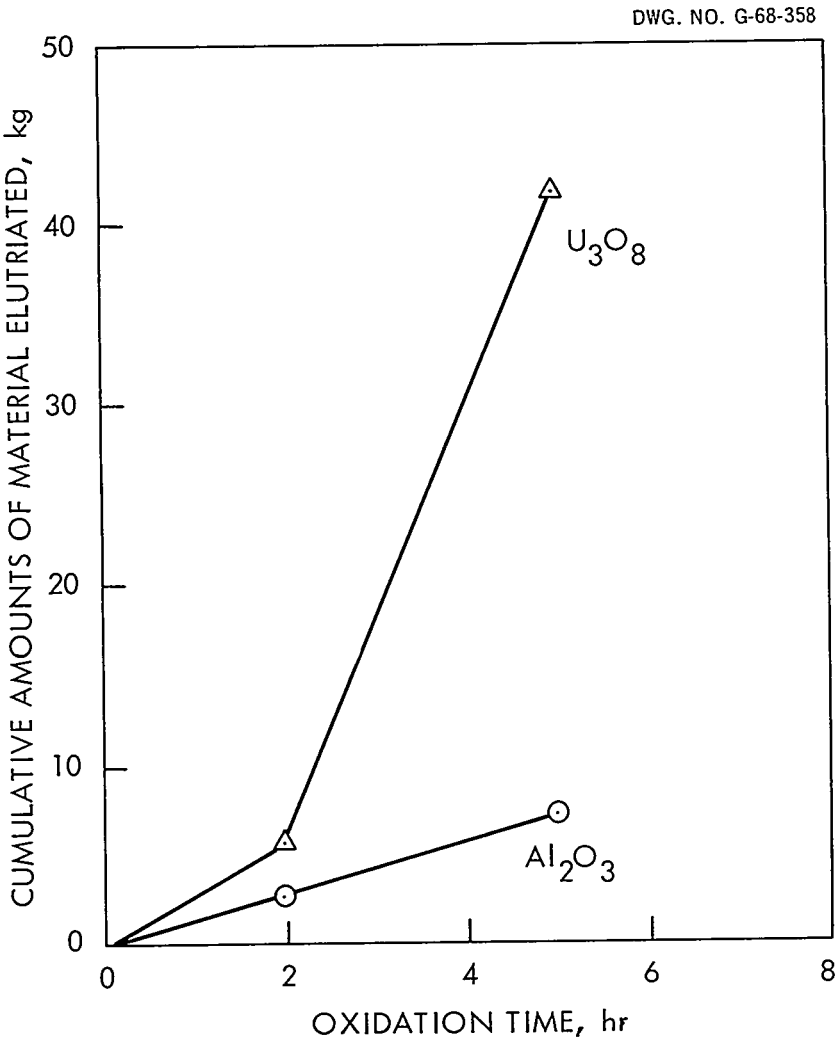
receiver was not dumped. Only about 1 kg of the original filter cooler bed was transferred to the receiver in this case. Moreover, past tests indicate that very little to no uranium and alumina is normally transferred from the reactor to the filter cooler up to this point.

The recovered material plus an additional 1.0 kg of new alumina was recharged to the filter cooler, and oxidation flows were started with 11% oxygen and a velocity of 1.8 ft/sec at 480°C and 0.8 psig in the 10-inch-diameter section of the reactor. All flows were shut off after 2 hours of oxidation, and the filter cooler and receiver were again emptied, while the contents (a mixture of U_3O_8 and alumina) were weighed and sampled. The filter cooler was then recharged with 11.4 kg of fresh alumina and oxidation was resumed for three more hours with 21% oxygen and a velocity of 1.4 ft/sec at 480°C and 2.9 psig to give a total oxidation time of 5 hours. Again, at the end of the test, the filter cooler and receiver contents were weighed and sampled.

During oxidation, 97.1% of the uranium charge was oxidized, 62.1% of the uranium charge was elutriated to the filter cooler, and 95.6% of the uranium dioxide pellet charge was comminuted to minus 35-mesh material. The cumulative weights of U_3O_8 and alumina elutriated as a function of oxidiation time are illustrated in figure 19.

Run UE-45. When temperatures in the pellet bed had stabilized at 480°C as the result of heatup, air was introduced into the reactor. The air flow was adjusted to give a comparatively high superficial gas velocity of 2.3 ft/sec based on average operating conditions of 450°C and 3.2 psig in the 10-inch-diameter section of the reactor. There was no observed temperature rise in the pellet bed even though air was used from the outset. When 2 hours of oxidation cycle had been completed, all flows were shut off, and the filter cooler was emptied. Only 5.0 kg of material was recovered even though the bottom of the vessel was rapped with a hammer several times. It was concluded that a portion of the cooler bed had bridged inside the vessel but the bridge had not been dislodged by rapping. A new alumina powder charge of 11.4 kg was added to the filter cooler, and the system was fluidized for 30 minutes with nitrogen at a velocity of 0.5 ft/sec in the 10-inch-diameter section of the reactor to try to loosen any bridged solids. The additional fluidization period was successful, and an additional 44.3 kg of material (a mixture of U_3O_8 and alumina) was recovered from the filter cooler and receiver.

The filter cooler was recharged with 11.4 kg of minus 48- plus 100-mesh alumina powder, and operations were resumed with nitrogen flow only. Air was not used for the remainder of the run so that the percentage conversion for the first 2 hours of oxidation could be determined. Continuation of the run at high gas velocities on the order of 2.2 ft/sec was thought to be desirable to obtain time versus elutriation data even though oxidation was not occurring. After 3 hours at 2.2 ft/sec based on operating conditions in the 10-inch-diameter section of the reactor, the nitrogen flow was shut off, and the filter cooler and receiver were emptied. The filter cooler was recharged with 11.4 kg of new minus 48- plus 100-mesh alumina powder. A nitrogen flow equivalent to a velocity of 2.1 ft/sec



U_3O_8 AND ALUMINA ELUTRIATION DURING OXIDATION IN UE-44

Figure 19

at 440°C and 1.7 psig in the 10-inch-diameter section was continued for an additional 3 hours to give a total elutriation time of 8 hours. There was no indication that the U_3O_8 elutriation was any different with nitrogen than with oxygen.

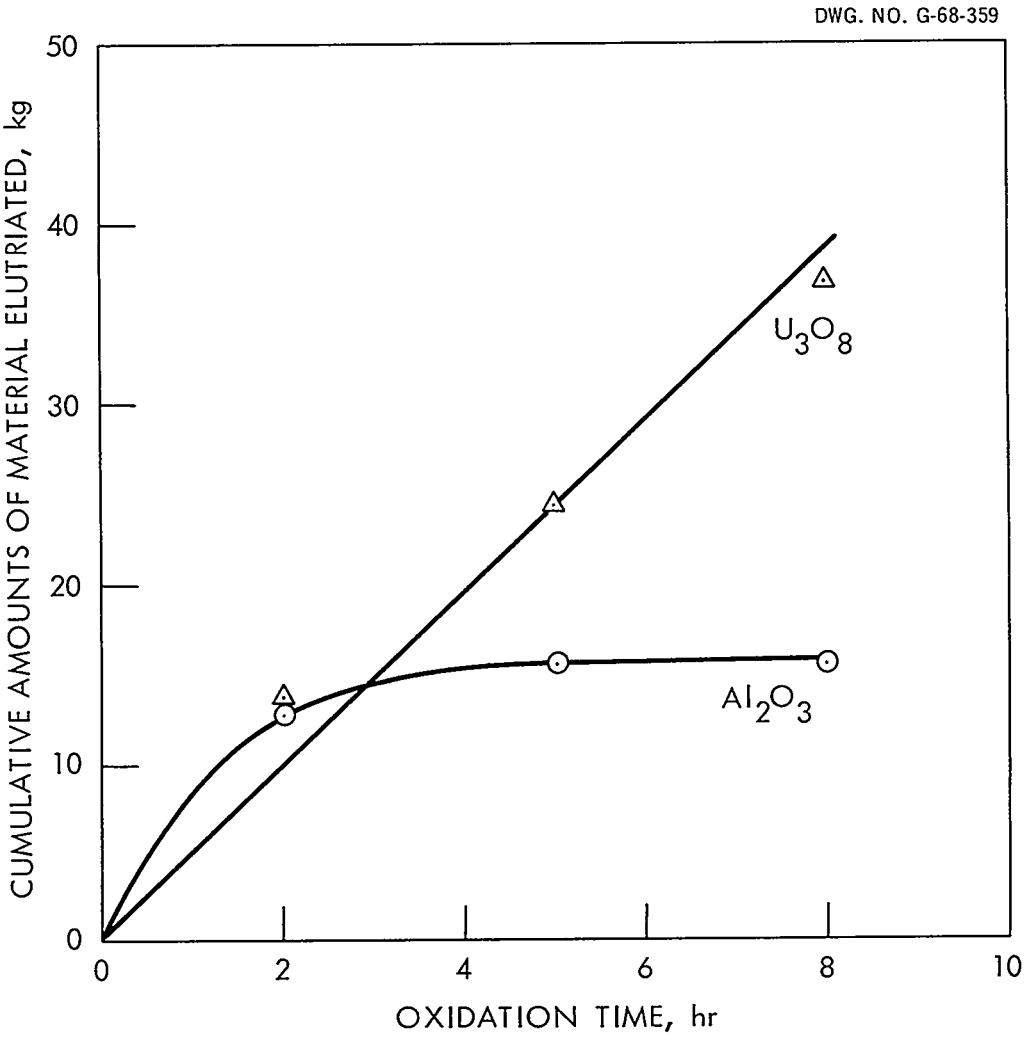
During the 8 hours at 2.1 to 2.3 ft/sec fluidizing velocities, 54.5% of the uranium charge was elutriated. The weights of material elutriated versus oxidation time are shown in figure 20. In the short oxidation cycle (2 hours) with 21% oxygen, the oxidation rate appeared to be about twice the rate which is achieved when 10.5% oxygen is used for the first 2 hours and is followed by 21% oxygen to complete the reaction. Chemical analyses indicated that 98.2% of the pellet charge was oxidized to U_3O_8; however, only 76.7% of the pellet charge was comminuted to minus 35-mesh material.

The bulk of the plus 35-mesh material was roughly 1/16 inch or less in diameter but some pieces were found which were as large as one-fourth to one-half the original pellet size. Most of the smaller pieces were reduced to powder when hand pressure was applied, but the large pieces could not be broken up in this manner. Normally, considerably well over 90% of the uranium dioxide pellet charge is comminuted to minus 35-mesh powder during oxidation steps of the usual 4 to 8 hours duration.

Run UE-46. This run was similar to UE-44 in that pellet oxidation was preceded by hydrogen chloride treatment; however, the hydrogen chloride treatment of the pellets was reduced from 4 to 1 hour, and the oxidation cycle was increased from 5 to 8 hours to obtain elutriation data for an extended tail-off period. The hydrogen chloride step was shortened to see if length of exposure to hydrogen chloride influences elutriation.

After charging had been completed, heatup to simulated declad temperatures of about 410°C was begun with the alumina bed fluidized with nitrogen. Hydrogen chloride flow was started when this temperature was reached. The flow was adjusted to obtain a 29% hydrogen-71% nitrogen mixture, and a velocity of 0.6 ft/sec in the 10-inch-diameter section of the reactor. The hydrogen chloride flow was checked by measuring the concentration of hydrogen chloride in the water from the scrubber. After 1 hour, the hydrogen chloride was valved out, and the system was purged with nitrogen while heating up to oxidation temperatures. The filter cooler and receiver were not emptied after the purging cycle, since data from runs UE-40 and -44 had indicated that no elutriation from the reactor occurred during the hydrogen chloride treatment and the subsequent nitrogen purge at the low velocities employed.

Oxidation was begun after 45 minutes of nitrogen purging, and the air and nitrogen flows were adjusted to give 10% oxygen and a velocity of 1.7 ft/sec in the 10-inch-diameter part of the reactor. Two hours after oxidation flows were begun, all flows were shut off, the filter cooler and receiver were dumped. The filter cooler was recharged with 11.4 kg of fresh minus 48- plus 100-mesh alumina powder, and oxidation was resumed for three additional hours at 21% oxygen and a flow corresponding to 1.4 ft/sec in



U_3O_8 AND ALUMINA ELUTRIATION DURING OXIDATION IN UE-45

Figure 20

the 10-inch-diameter part of the reactor based on average operating conditions. At the end of this time, the filter cooler and receiver were again emptied and recharged as before, and oxidation was continued for an additional 3 hours to give a total oxidation time of 8 hours. During this period, the oxygen concentration was maintained at 21%, and the velocity was kept at 1.5 ft/sec in the 10-inch-diameter section of the reactor. No operational problems were encountered in the run.

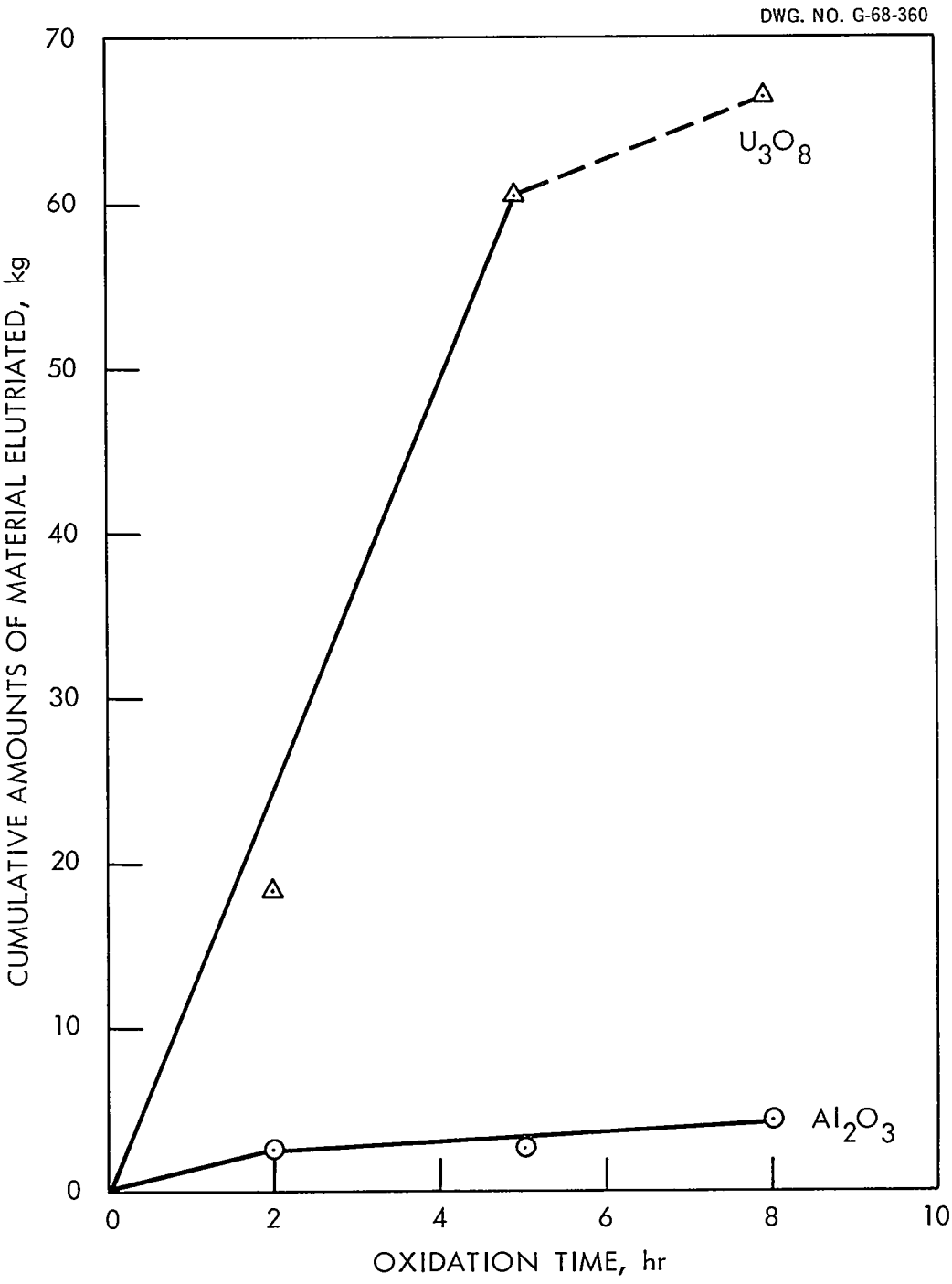
For the total 8-hour oxidation cycle, 96.0% of the uranium charge was oxidized to U_3O_8, 98.3% of the uranium charge was elutriated, and 98.3% of the pellet charge was comminuted to minus 35-mesh material. After 5 hours, 89.3% of the uranium charge had been elutriated. A plot of U_3O_8 and alumina elutriation versus oxidation time is given in figure 21. For the same time in UE-44, only 62.1% of the uranium charge was elutriated. This may indicate that there is an optimum time for exposure to hydrogen chloride from the standpoint of maximizing elutriation, with this time being less than 5 hours. Data are considered too fragmentary to draw conclusions.

Run UE-47. When the element was charged, the top was located about 8 inches below the gas exhaust line. Alumina powder was added after the element was in place. When static, the alumina bed was about 2 feet deep.

The alumina powder was fluidized with nitrogen, and heatup was started with a gas velocity of 0.5 ft/sec. The declad step was begun when the temperature in the bed leveled out at 400°C. The gas concentration was kept at 25% hydrogen chloride and 75% nitrogen during the first 1/2 hour and at 30% hydrogen chloride and 70% nitrogen for the next 2-3/4 hours. The gas velocity in the 10-inch zone was maintained at 0.9 ft/sec. It took 1 to 1-1/2 hours for the reaction to start, as evidenced by a rise in the temperature of the element and the appearance of the scrubber effluent in that time period. The delay in the reaction may have been associated with some kind of treatment, such as autoclaving, to which the zircaloy rods had been exposed; unfortunately, the previous history of the tubes has not been established.

About 3-1/4 hours after the hydrogen chloride decladding was started, white vapor was observed escaping from the liquid drain line from the scrubber. Since the cause for this new occurrence was not apparent, all flows were shut off. Upon inspecting the system, a yellowish paste weighing about 1.0 kg was found on the roof of the pilot plant directly below the gas exhaust line from the scrubber. Chemical analysis of the paste indicated 24.3 weight percent zirconium and 15.6 weight percent chloride. The run was temporarily interrupted until the scrubber gas exhaust line could be taken down for inspection. It was considered possible that the line might be partially plugged with desublimed zirconium tetrachloride because of incomplete hydrolysis in the scrubber, but surprisingly enough, no plug was found.

During the period that the pipe was removed, the reactor was opened to inspect the partially reacted fuel element. Twelve of the eighteen fuel rods had dropped out of the top bracket, and the lengths of these twelve



U_3O_8 AND ALUMINA ELUTRIATION DURING OXIDATION IN UE-46

Figure 21

tubes had been reduced to about 6 feet. Appreciable reaction was apparent on the lower 8 inches of the rods that had dropped out. All of the cluster wire wrap and cluster bands had been reacted completely, and calculations indicated that about 45% of the cladding had been volatilized from the reactor. The end brackets were still intact, and the top bracket was removed from the reactor before the top of the reactor was reinstalled. Figure 22 shows a photograph of the element at this time. Table XIX gives temperatures in the element and the fluid surrounding the element for the first 2-3/4 hours of the decladding cycle. As can be seen in this table, the maximum temperature difference between the element and the fluid was 61°C and was observed at the top of the element above the fluidized bed. The maximum temperature differences at the bottom and 32 inches up from the bottom of the element, i.e., positions where the fluidized bed was in contact with the element, were 22 and 25°C, respectively. Each time readings were taken after the first 1-1/4 hours of operation, the fuel element and fluid-bed temperatures were found to be the highest at the thermocouple 32 inches up from the bottom. This may mean that the maximum reaction is taking place above the bottom, the point of initial contact between the hydrogen chloride and the zircaloy.

TABLE XIX

TEMPERATURES DURING DECLADDING OF THE PRTR FUEL ELEMENT, UE-47

Hydrochlorination Time, hr	Temperature, °C, at Position* Noted						Temperature Difference, °C		
	Fuel Element			Fluid-Bed Gas Space					
	A	B	C	A	B	C	A	B	C
0	393	393	393	393	393	393	0	0	0
0.25	396	396	402	393	393	399	3	3	3
0.75	399	396	402	393	393	399	6	3	3
1.25	404	407	427	393	404	399	11	3	28
1.75	421	429	460	399	421	404	22	8	54
2.25	427	443	477	416	432	416	11	11	61
2.75	432	468	471	416	443	432	16	25	39

* Position A corresponds to the bottom of the element, B to about 32 inches up from the bottom, and C to the top of the element as positioned in the reactor; i.e., above the top level of the fluidized bed.

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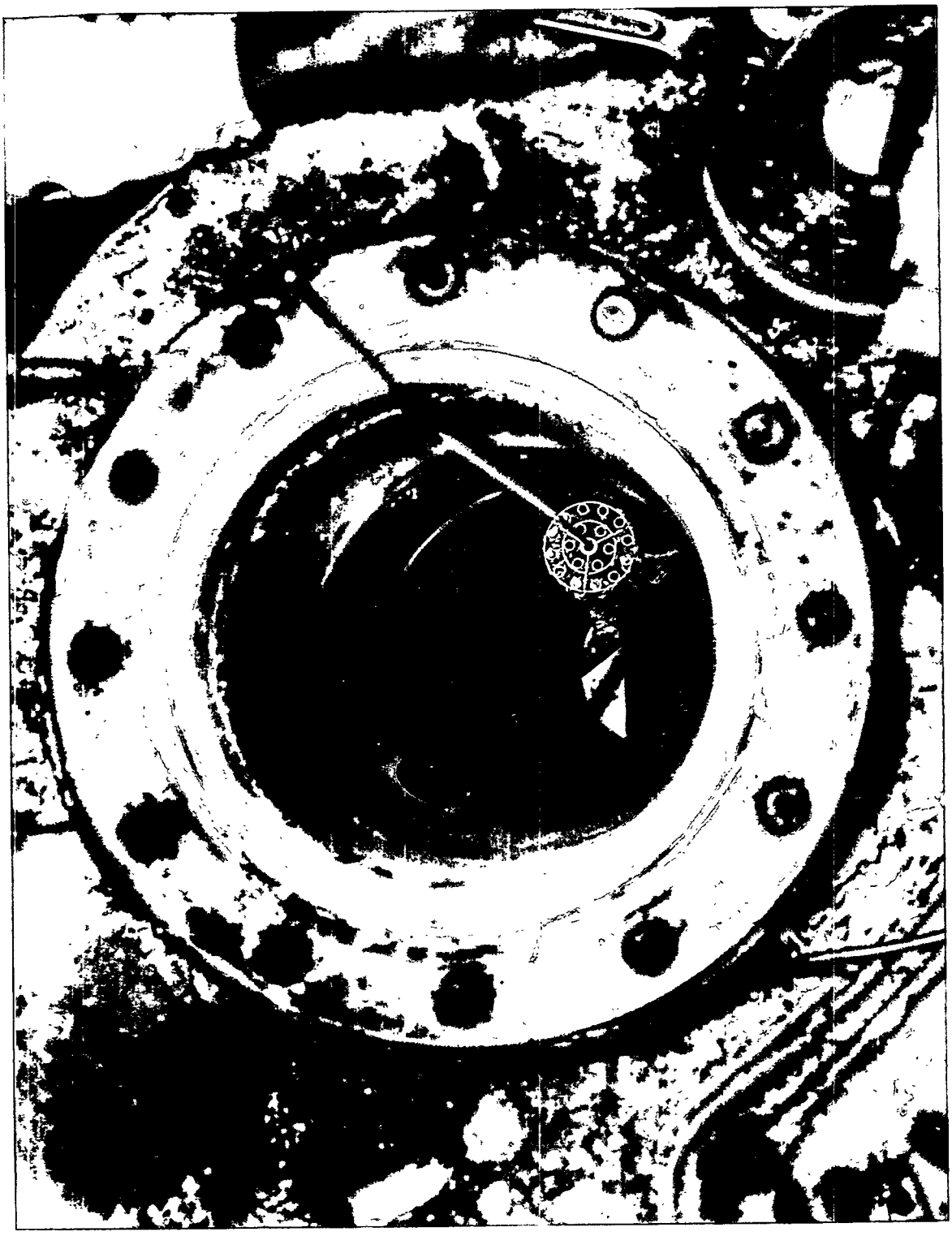

PRTR FUEL ELEMENT AFTER 3-1/4 HOURS OF EXPOSURE TO HYDROGEN CHLORIDE IN UE-47

Figure 22

The reactor was again closed and was heated up to decladding temperature with the bed fluidized with nitrogen at 0.5 ft/sec. When the temperatures had stabilized, flows were adjusted to give 22% hydrogen chloride and a velocity of 0.8 ft/sec based on the average operating temperature and pressure. The scrubber effluent became milky within 5 minutes, thus indicating that reaction was in progress. The hydrogen chloride concentration was increased to 40% 30 minutes after decladding was resumed. The run appeared to be proceeding smoothly; however, vapor was again observed escaping from the liquid drain line from the scrubber. The gas flow was reduced to give a velocity of 0.5 ft/sec while the hydrogen chloride concentration was maintained at 40%, since it appeared that the scrubber was not large enough to handle the flow rate required for a 0.8 to 1.0 ft/sec velocity in the 10-inch zone. After the flow was reduced, no additional problems were observed; the declad cycle was terminated after a cumulative reaction time of 7.55 hours.

Following decladding, the system was purged with nitrogen, the filter cooler and receiver were emptied, the filter cooler was recharged with 11.4 kg of fresh alumina, and heatup to oxidation temperature was begun with the bed fluidized with nitrogen. When the temperature in the fluidized bed reached 480°C, air flow was started. The oxygen concentration was kept at 21%, and the gas velocity was kept at 1.3 ft/sec. The gas was cut off, and the filter cooler and receiver were emptied after 2, 5, and 8 hours of oxidation to obtain elutriation data. Fresh alumina powder, weighing 11.4 kg, was recharged to the filter cooler each time it was emptied. Oxidation was terminated after 8 hours.

By chemical analysis, conversion of the uranium dioxide charge to U_3O_8 was only 93.5% complete; however, all of the uranium was comminuted to minus 35-mesh powder. The elutriated material contained the equivalent of 88.0 weight percent U_3O_8, with the amount of uranium elutriated corresponding to 90.3% of the uranium charged to the reactor. Only 10.5% of the alumina powder charge to the reactor was elutriated. The U_3O_8 and alumina elutriation during the progress of the oxidation are plotted in figure 23*.

On the other hand, the results for the declad cycle were not as good as was expected. The overall hydrogen chloride utilization was 18.8%, and only 83.8% of the zirconium charge was reacted during the 7.55-hour declad cycle. About 0.5 kg of unreacted zircaloy tubing and 1.3 kg of end caps were found in the bed after oxidation. Actually, none of the original thirty-six end caps were completely reacted. Figures 24 and 25 show these unreacted pieces. The progress of the zirconium reaction and the hydrogen chloride usage with time is given in figure 26.

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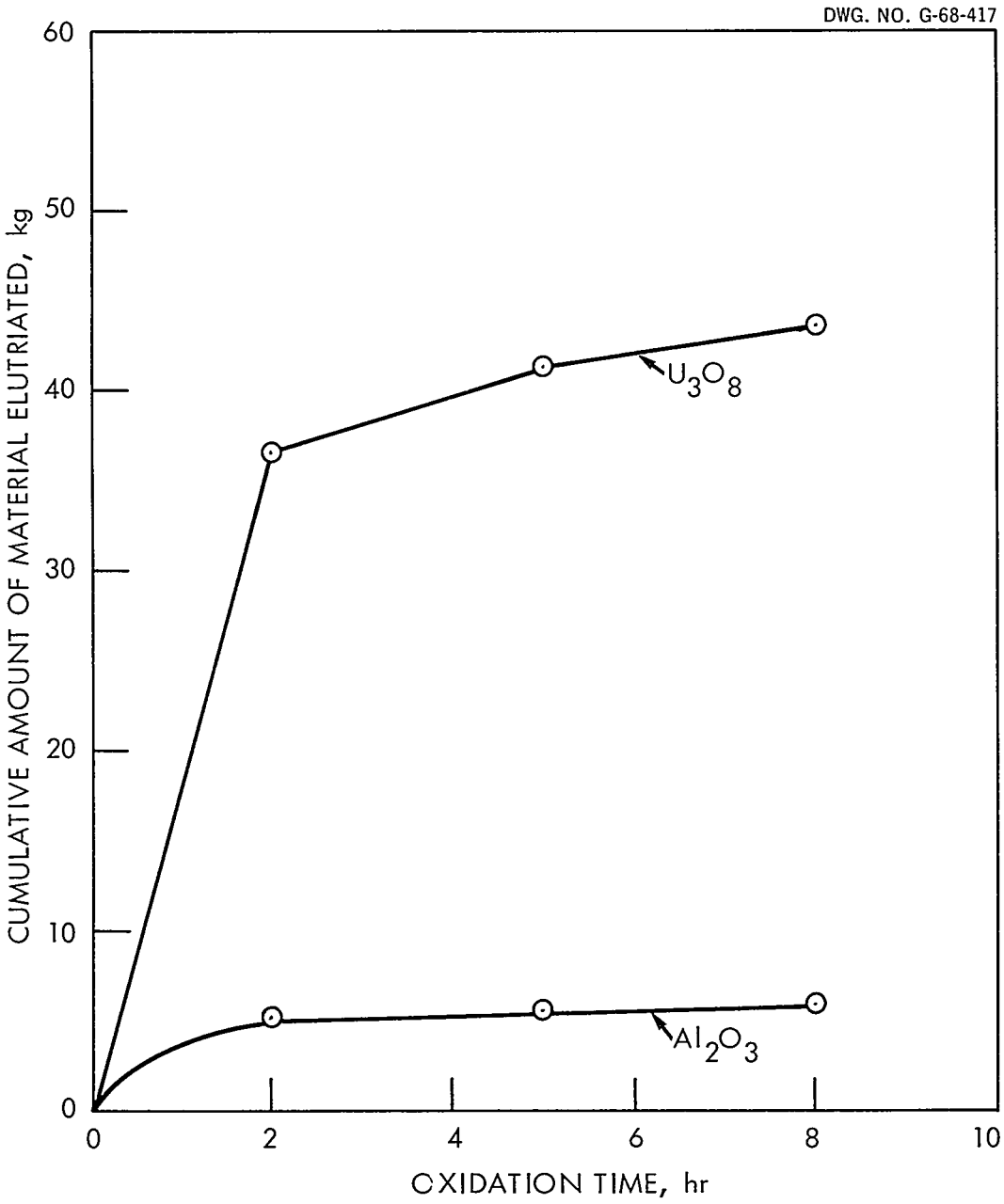
* In a later decladding experiment in the filter test loop, it was concluded that the vibratory compacted uranium dioxide is largely pulverized during the decladding step. The large amount of U_3O_8 elutriated in the first 2 hours of the UE-47 oxidation phase supports this conclusion.



U_3O_8 AND ALUMINA ELUTRIATION DURING OXIDATION IN UE-47

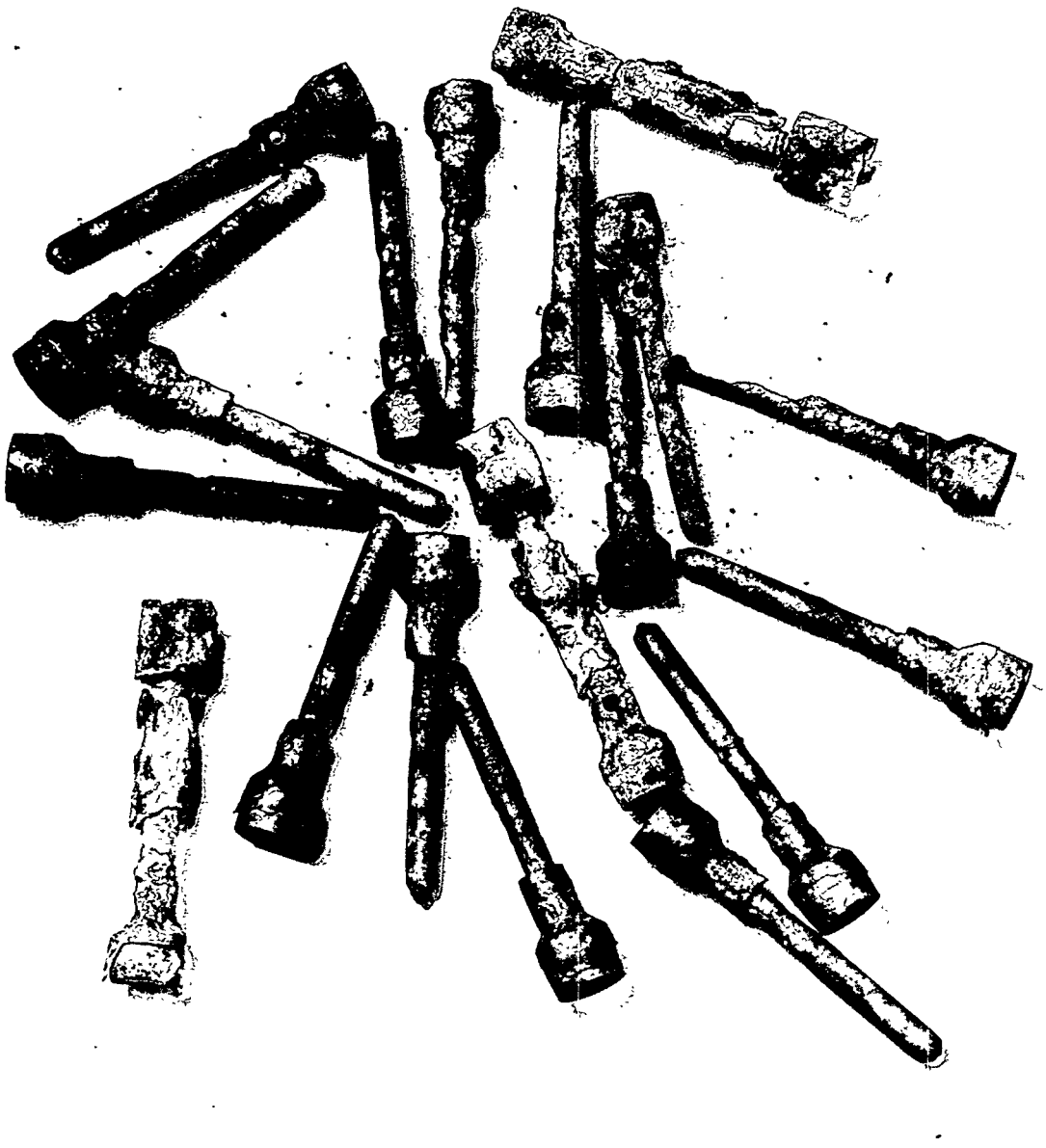
Figure 23

PHOTO NO. PH-68-44

TYPICAL UNREACTED ZIRCALOY TUBING REMOVED FROM REACTOR AFTER OXIDATION CYCLE IN UE-47

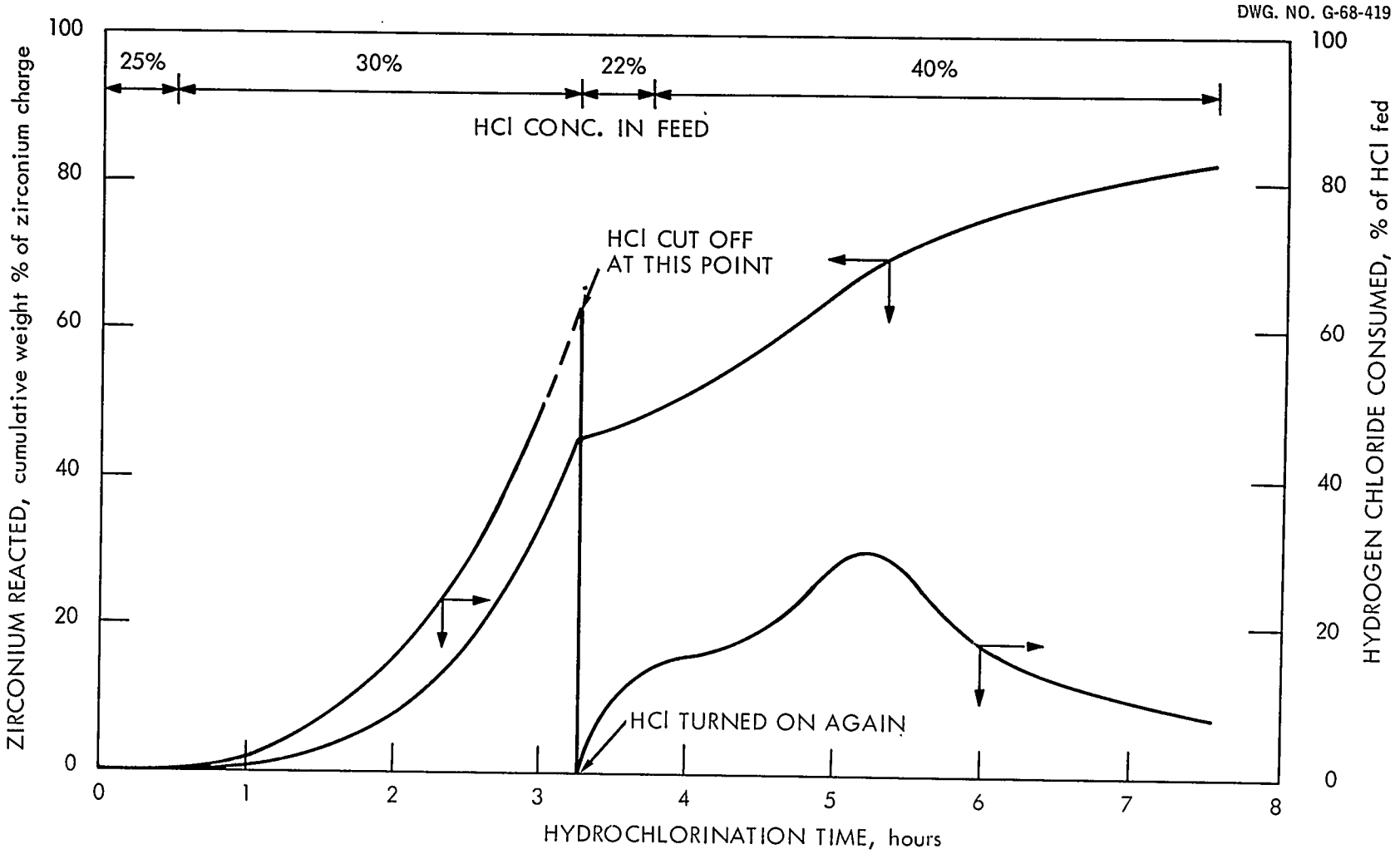
Figure 24

PHOTO NO. PH-68-45



TYPICAL UNREACTED END CAPS REMOVED FROM
REACTOR AFTER OXIDATION CYCLE IN UE-47

Figure 25



ZIRCONIUM REACTED AND HCl CONSUMED IN RUN UE-47

Figure 26

If the hydrochlorination time had been extended, more zircaloy would undoubtedly have been reacted. The run was intentionally limited to 7.55 hours to observe the effects on subsequent oxidation when unreacted pieces remain in the fluid bed after decladding.

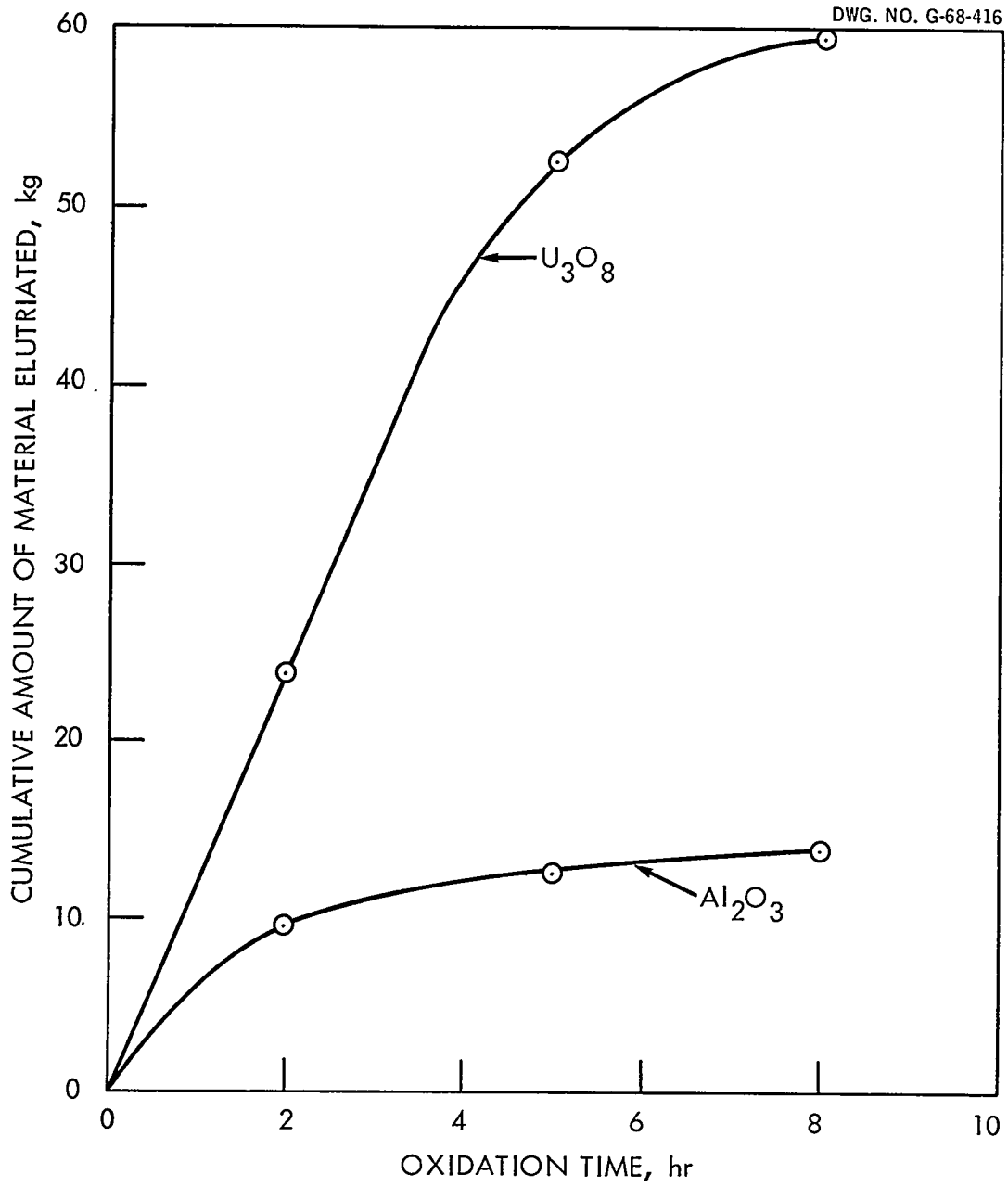
Run UE-48. In a previous run, UE-45, Westinghouse normal assay solid cylindrical uranium dioxide pellets were processed with air at 455°C for 2 hours to determine if 2 hours of oxidation with that high an oxygen concentration was sufficient for high conversion. Nitrogen was used for the last 6 hours of the run to obtain elutriation data. While 98.2% of the pellet charge was oxidized, only 76.7% of the uranium charge was comminuted to minus 35-mesh material. Since comminution was low in UE-45, it was decided to study the oxidation reaction with the Westinghouse pellets further by extending the reaction time with air to 8 hours.

After the system was charged for run UE-48, the alumina powder in the reactor was fluidized with nitrogen and the entire pellet bed was heated to 470°C. Sufficient air flow was started when this temperature was obtained to give a velocity of 1.8 ft/sec based on average operating conditions in the 10-inch-diameter section. These conditions were maintained for 2 hours, at which time, all flows were shut off, and the filter cooler and receiver were emptied. Oxidation was resumed for 3 hours more, with air at the same velocity, after the filter cooler had been recharged with 11.4 kg of fresh minus 48- plus 100-mesh alumina powder, and then the flows were again shut off to dump the filter cooler and receiver for the second time. The filter cooler was recharged with 11.4 kg of alumina powder, and oxidation was continued for a final 3-hour period to give a total oxidation time of 8 hours. No problems were encountered in the run.

By chemical analysis, the uranium dioxide pellet charge was 98.3% oxidized; however, only 88.7% of the material was converted to minus 35-mesh powder. With EGCR annular pellets, usually more than 95% of the uranium is comminuted to minus 35-mesh. Thus, the results from this run and from run UE-45 suggest that the solid cylindrical pellets are harder to break up during oxidation than are the EGCR pellets. During the 8 hours of oxidation, about 88.7% of the uranium charge was elutriated; i.e., essentially all of the minus 35-mesh material. This is the largest amount of uranium ever elutriated during the ORGDP runs which involved oxidation only. The material that was elutriated contained 81.1% U_3O_8. The elutriation profile for this run is given in figure 27.

Run UE-49. After charging had been completed, the alumina powder was heated to 480°C, the air flow was started, and the nitrogen flow was valved out. Pellet charging was begun 3 hours 15 minutes after the air flow was started and was continued for the next 1 hour 45 minutes. During this time, 31.8 kg of EGCR pellets was charged to the reactor through the hold volume in about 1.4 kg batches.

When the pellet charger was loaded to capacity, i.e., with about 4.0 kg of EGCR pellets, it was difficult to get the pellets to fall out into the reactor, apparently because of bridging. Even with 1.4 kg batches, it



U_3O_8 AND ALUMINA ELUTRIATION DURING OXIDATION IN UE-48

Figure 27

was necessary to beat on the pellet charger with a hammer to move the pellets out. The hammering caused the unions on the ball valves to loosen, and these had to be tightened during the charging to prevent powder leaks.

Over the course of the charging period, the pressure drop across the reactor rose from 6.0 to 6.4 psi. No further increase was observed during the remainder of the run. The velocity in the 10-inch-diameter section of the reactor was kept at 1.7 ft/sec and the oxygen concentration at 21% throughout the run. Total oxidation time was 9 hours. Analyses of the bed materials indicated that 98.5% of the uranium charge was comminuted to minus 35-mesh material and that 97.8% of the uranium charge was oxidized. During the oxidation cycle, 63.9% of the uranium charge and 6.5% of the alumina were elutriated to the filter cooler.

Run UE-50. As in previous runs, heatup was started with the alumina bed in the 10-inch-diameter zone. An attempt was made with the nitrogen flow on to empty the alumina from the filter cooler before oxidation started. Even though the flange on the bottom of the filter cooler was rapped with a hammer several times, no powder came out. The gas flow was stopped and a second attempt was made to empty the alumina but still no material was recovered. Nitrogen was again introduced, and another 11.4 kg of alumina was placed in the filter cooler, hopefully to break up a possible bridge. This technique was successfully used in run UE-45. The alumina was easily charged to the filter cooler even though nitrogen was flowing through the system. A third try to empty the filter cooler contents with the nitrogen flow on was successful after 10 minutes of fluidization and considerable hammering, and 23.3 kg of alumina was recovered.

The filter cooler was recharged with 11.4 kg of the recovered alumina powder, and the oxidation step was begun with air. The temperature in the pellet zone increased to 538°C within about 5 minutes, but cooling with air in the external coils reduced the temperature to 482°C, the desired level, in 15 minutes. Pellet charging had been started when air flow was resumed, and 13.6 kg of pellets was charged to the reactor in about 2.3 kg batches during the first half-hour of oxidation. A small powder leak developed at the union on the bottom valve of the pellet charger, probably because of the hammering necessary to get the pellets to fall out. After the 13.6 kg had been charged to the reactor, the air flow was stopped, and the leak was eliminated by tightening.

Pellet charging was continued, and nine additional 13.6 kg loads of pellets were added to the reactor at 1-hour intervals. Each time, it took about 15 minutes to dump the contents of the charge volume into the reactor.

The filter cooler was emptied and recharged with 11.4 kg of fresh alumina powder after 3, 6, 9, 12, and 15 hours of oxidation.

The run was terminated after 15-1/2 hours. The oxygen inlet concentration and the gas velocity in the 10-inch-diameter section were kept at 21% and 1.6 ft/sec, respectively, throughout the run. The nominal temperature in the 10-inch section was near 460°C. No reactor plugging problems were

observed in the run. The reactor pressure drop ranged from 4.2 to 7.8 psi with the nominal value near 4.8 psi. Pellet and alumina charging were successful; however, the dumping of the filter cooler contents with gas passing through the system was judged unsuccessful, since only 23.6% of the material that was elutriated during oxidation was recovered during the dumping attempt. The rest of the elutriated material was taken out of the filter cooler after the cooldown period.

During oxidation, 99.2% of the pellet charge was oxidized, and 25.7% of the uranium was elutriated to the filter cooler. Screen analysis indicated that only 71.4% of the uranium charge was comminuted to powder smaller than 35 mesh.

Run UE-51. This run was the first test in which an oxygen concentration greater than 21% was used. Oxidation of a single charge of Westinghouse normal-assay pellets was undertaken for 3 hours using a combined air-oxygen feed mixture with an oxygen concentration of 40%.

Nitrogen was used to fluidize the bed during heatup. When the temperature in the bed reached 482°C, 40% oxygen flow was started. An immediate increase in bed temperature was observed, and the temperature reached a maximum of 538°C, five minutes after oxygen flow was begun. Forced-air cooling through the external coils was used for the remainder of the run to keep the bed temperature at the desired level of 482°C. The pressure drop through the reactor fluctuated between 2 and 8 psi during the first hour of operation, and bed plugging tendencies were noted, apparently having been brought about by a buildup of power during the rapid reaction. After the first hour, the pressure drop leveled out at a nominal 7 psi, and there were no further indications of plugging or abnormal pressure variations.

Analysis of final bed materials obtained after the 3-hour oxidation cycle indicated 95.9% of the pellet charge was oxidized to U_3O_8; however, only 55.2% of the uranium charge was comminuted to minus 35-mesh material. Uranium dioxide elutriated to the filter cooler accounted for 33.7% of the uranium charged.

Run UE-52. This run was undertaken to study the combined effects of semicontinuous pellet charging and an oxygen concentration of 40% during the oxidation step. After the initial charge, Westinghouse normal-assay pellets weighing 136.2 kg were added semicontinuously to the reactor in 27.2 kg increments during the first 5 hours of the run.

Since there was a rapid increase in bed temperature in the previous run, once the 40% oxygen was introduced, the pellet bed was only heated to 427°C instead of the desired 482°C with the thought that the reaction heat would make up the difference. When the pellet zone temperature stabilized at 427°C, 40% oxygen flow was substituted for the nitrogen. The temperature in the bed increased to 482°C within 10 minutes. Semicontinuous charging was begun 1/2 hour after startup and 27.2 kg of the pellets were put in the reactor over the next 1/2 hour. The bed temperature increased to 504°C during this time. The second pellet charging was

started 1-1/2 hours after startup, and 27.2 kg of pellets was dropped into the bed between 1-1/2 to 2 hours. By this time, the pressure drop through the bed had increased to 9.5 psi and there was no indication that the pressure drop would level out or decrease. The bottom of the reactor was rapped with a hammer several times to open up the bed, and the pressure drop was reduced to 6 psi. Pellet charging was continued, and three additional 27.2 kg loads were put into the reactor at 1-hour intervals. The charging process took about 1/2 hour in each case.

Oxidation was terminated after 10 hours. The nominal gas velocity was near 1.5 ft/sec for the run. Although abnormal fluctuations in the reactor pressure drop were observed frequently in the run, the pressure drop was kept within reasonable bounds by rapping the bottom of the reactor with a hammer. Temperature control was good throughout the run.

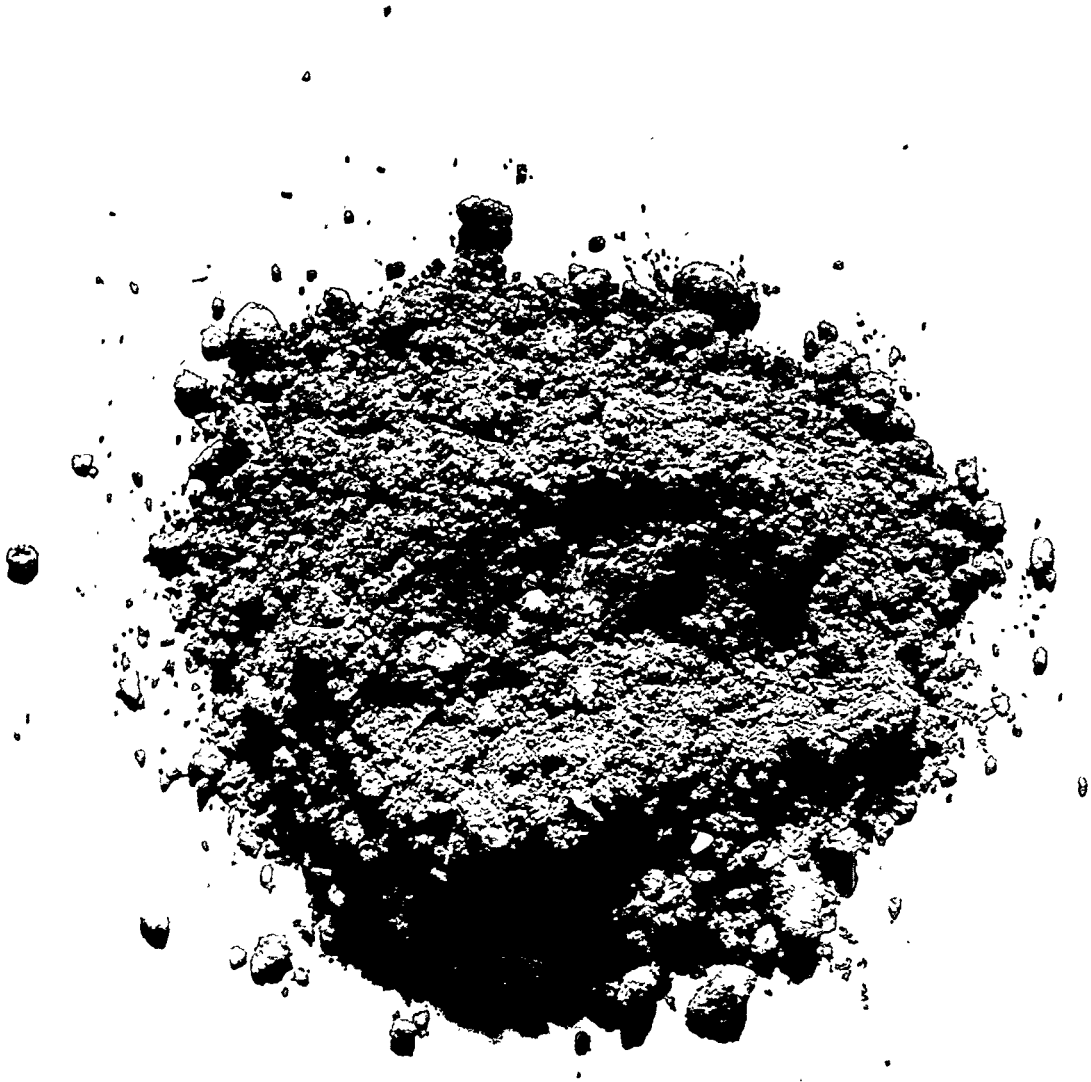
When the run was terminated, the system contents were kept fluidized with nitrogen, and the system was cooled using the external air cooling. When cooldown was completed, the material in the reactor would not drain out through the bottom valve; therefore, the powder was taken out via the top of the reactor using a vacuum system. Once the powder was removed, the balls were drained from the bottom of the reactor by gravity discharge, while the remaining material had to be taken out through the top of the vessel with a vacuum system.

In the oxidation step, 99.5% of the uranium dioxide was oxidized, while only 75.1% of the uranium was converted to material smaller than 35 mesh. The plus 35-mesh powder shown in figure 28 consisted primarily of powder agglomerates, some of which could be reduced in size when light pressure was applied. Only 29.3% of the total uranium charge was elutriated to the filter cooler during the 10-hour oxidation test.

Run UE-53. Since only 55.2% of the uranium charge, i.e., Westinghouse pellets, had been comminuted to minus 35-mesh material in UE-51, similar operating conditions were employed in this run with EGCR pellets to determine if comminution is influenced by pellet source and/or geometry. The total oxidation time was 3 hours, and 40% oxygen in the feed gas was used from the outset.

The entire pellet bed was heated to 482°C. Once this temperature had been stabilized, the oxygen concentration was adjusted to 40%. As in UE-51, a rapid increase in pellet bed temperature was observed when the oxygen flow was begun. The temperature in the pellet bed increased from 482 to 560°C within 5 minutes, and air cooling with the external coils was used to bring the temperature down. The pressure drop through the reactor remained constant at 4.7 psi during the first 1/2 hour of operation and gradually increased to 5.0 psi over the next 2-1/2 hours. The run was terminated after 3 hours. Throughout oxidation, the inlet oxygen concentration and the 10-inch-diameter section velocity were kept at 40% and 1.7 ft/sec, respectively. No plugging tendencies were observed during the run, and the bed temperature was controlled with external cooling coils.

PHOTO NO. PH-68-564



PLUS 35-MESH MATERIAL RECOVERED FROM REACTOR AFTER OXIDATION STEP IN UE-52

Figure 28

Analysis of bed materials taken from the system after the run indicated that 99.1% of the EGCR pellet charge was oxidized, 44.8% of the uranium charge was elutriated, and that 95.5% of the uranium had been comminuted to minus 35-mesh material. The plus 35-mesh material shown in figure 29 contained hard pieces of oxidized pellets and fragments of alumina balls. The results of this test strongly suggest that EGCR pellets are easier to comminute to small sized material than are the Westinghouse solid cylindrical pellets. This fact is also confirmed by data obtained in the oxidation tests which have been made with 10-inch-diameter pellet beds at lower oxygen concentrations. For example, the comminution of EGCR fuel material has ranged from 90 to 99%, excluding the semicontinuous runs and the tests in which hydrogen chloride gas was used to volatilize zirconium or to simulate the decladding cycle. On the other hand, for the same kind of test, with the solid cylindrical Westinghouse pellets, comminutions of 55 to 89% were obtained.

Run UE-54. The bottom of the element was located approximately 1 foot above the top of the transition section. The depth of the alumina bed, when static, was 1 foot 11 inches and approximately 2 feet 8 inches of the element extended above the top of the alumina. The element was fitted with a thermowell lengthwise through the center of the tube array, and thermocouples were placed at each end and at the center of the element.

After charging had been completed, the bed was fluidized with nitrogen and heated to 425°C. The gas preheater outlet and the filter cooler outlet temperatures were held at about 315°C. Decladding was undertaken with stepwise increases in hydrogen chloride concentration and consisted of 4 hours with 20%, 4 hours with 35%, and 6 hours with 60% hydrogen chloride in nitrogen. Hydrogen was not used in the feed gases. The superficial gas velocity was kept nominally at 0.7 ft/sec during the 14-hour declad step.

The liquid effluent from the scrubber became opaque about 30 minutes after the 20% hydrogen chloride was introduced into the reactor. A significant slowdown in the reaction was not observed until after 13-1/2 hours, when the scrubber water began to clear up.

The three thermocouples placed within the element indicated temperatures which were somewhat higher than those of the bed itself. The maximum temperature, 560°C, or 100°C above the bed temperature, was measured in the middle of the element. Reaction and temperature control were judged good; furthermore, no problems were encountered with the scrubber at this velocity*.

The system was purged with nitrogen for an hour after the hydrogen chloride step, and the bed was heated to 482°C. Before oxidation was begun, the

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* In run UE-47, the flow capacity of the scrubber was exceeded when gas was passed through the 10-inch-diameter section of the reactor at 0.8 to 1.0 ft/sec (see pp. 75 and 79 of this report).

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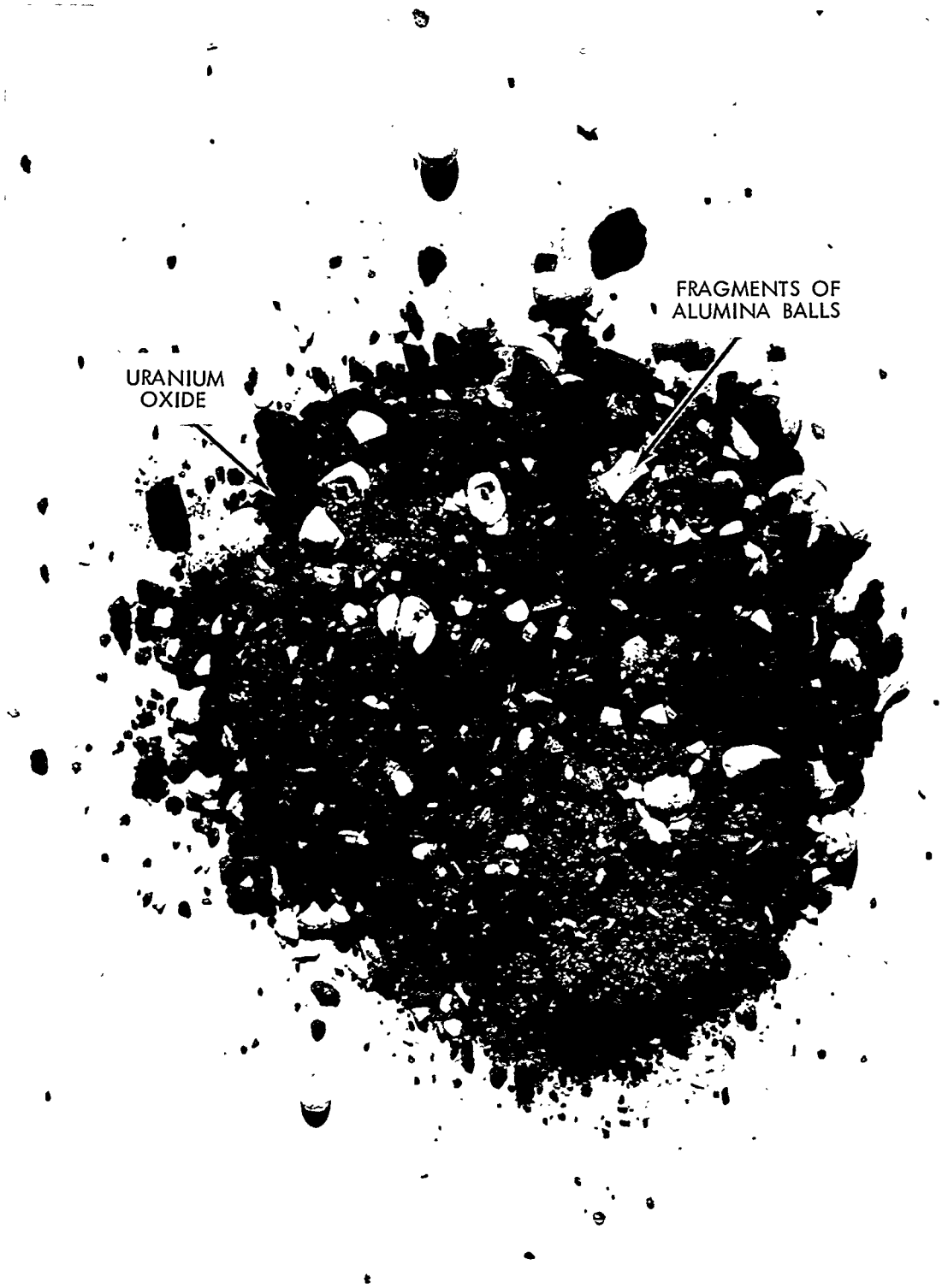

PLUS 35-MESH MATERIAL RECOVERED FROM REACTOR
AFTER OXIDATION STEP IN UE-53

Figure 29

filter cooler was emptied and recharged with 11.4 kg of fresh alumina. Material weighing 8.8 kg was recovered, and only 0.04 kg was larger than 35 mesh. Chemical analysis indicated that both the plus and minus 35-mesh fractions contained 0.19 weight percent zirconium.

The oxidation cycle consisted of 4 hours with an oxygen concentration of 40%. An increase in bed temperature occurred shortly after the oxidation step was started, the maximum temperature being 537°C. The pressure drop through the bed stayed constant during the cycle, and plugging tendencies were not observed. The superficial gas velocity was held at 1.5 ft/sec throughout oxidation.

Oxidation was judged good both from the operational standpoint and from results obtained on the final bed materials. Various materials recovered from the reactor and filter cooler after the run are shown in figure 30. Chemical analysis and material balances indicated 97.1% of the uranium dioxide was oxidized to U_3O_8, 88.6% of the uranium charge was elutriated, and 99.4% of the uranium was converted to material smaller than 35 mesh. The pulverization of 99.4% compared well with the 100.0% result obtained in the first semiworks test with a simulated fuel assembly, UE-33. Both the simulated fuel assemblies contained solid cylindrical fuel pellets; thus, the good comminutions obtained in these two runs suggest that decladding significantly improves pellet degradation to fine sized material during the subsequent oxidation step. The uranium elutriation rate of 22.2% per hour was the highest rate obtained in the ORGDP studies and confirmed the fact that decladding preceding oxidation also influences the rate of elutriation. In figure 30, the unusually large fraction of alumina ball fragments in the plus 35-mesh material taken from the reactor is ascribed to the prolonged reuse of balls in semiworks runs.

Results for the declad cycle indicated that 92.6% of the zircaloy charge was volatilized. Unreacted tie rods, shown in figure 30, weighing 1.5 kg, constituted the major portion of unreacted zircaloy. Bed analysis indicated that the minus 35-mesh and plus 35-mesh fractions of the reactor bed both contained 0.17 weight percent zirconium, and that the final filter cooler material had a zirconium content of 0.19 weight percent. The overall hydrogen chloride utilization was about 25% of the hydrogen chloride feed, and the maximum instantaneous utilization was slightly over 60%, as shown in figure 31.

In figure 32, the percentage of the uranium charge elutriated per hour of oxidation time is plotted versus the square of the time-weighted superficial velocity in the 10-inch-diameter section of the reactor. Two lines are shown, one for the runs in which the hydrogen chloride decladding or hydrogen chloride treatment preceded the oxidation step* and the other for runs involving oxidation only. The latter plot was originally

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* Data for UE-24 have been omitted, since extremely low oxygen concentrations (1 and 3%) were used.

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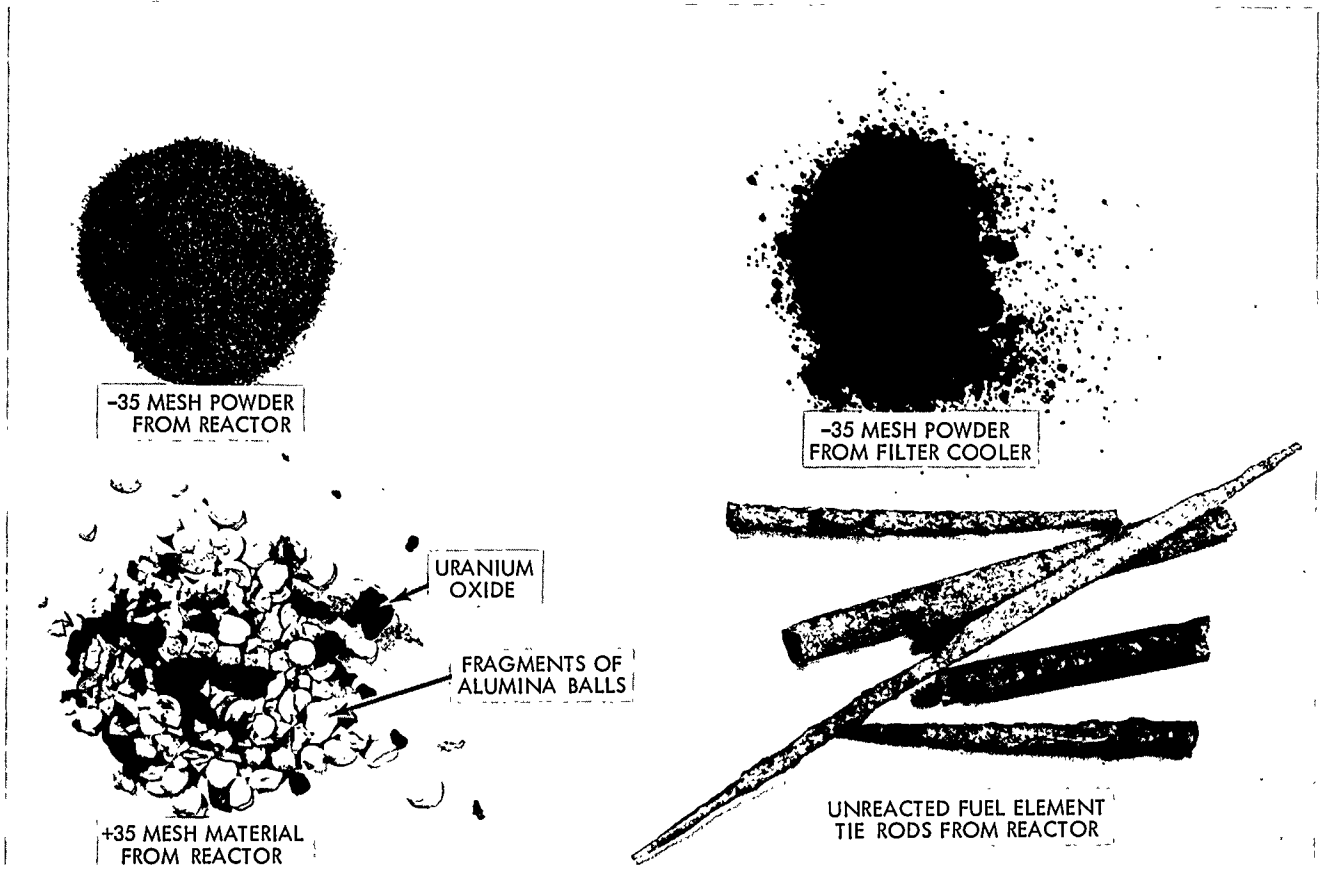
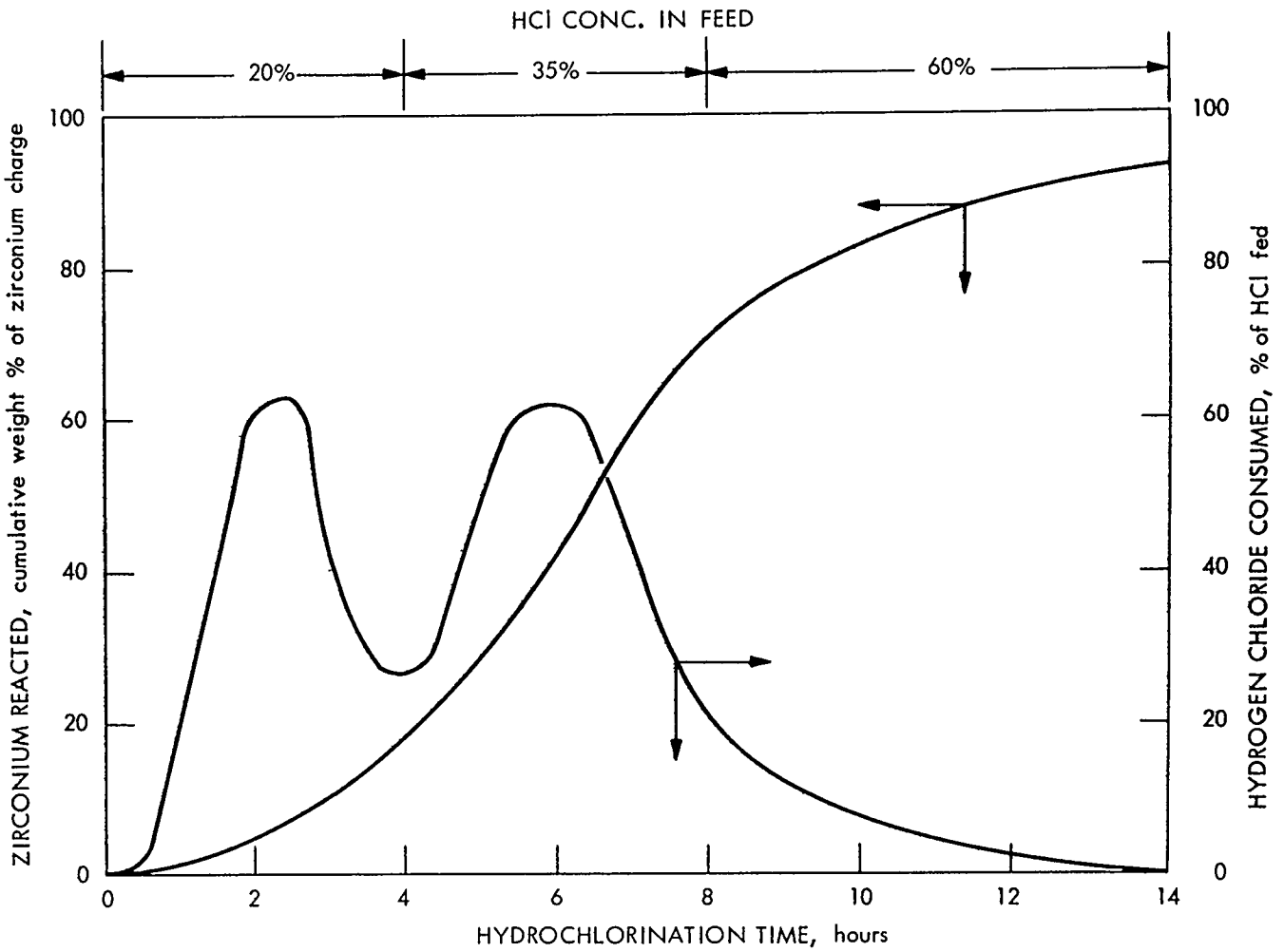


TYPICAL MATERIALS RECOVERED FROM SEMIWORKS SYSTEM AFTER OXIDATION IN UE-54

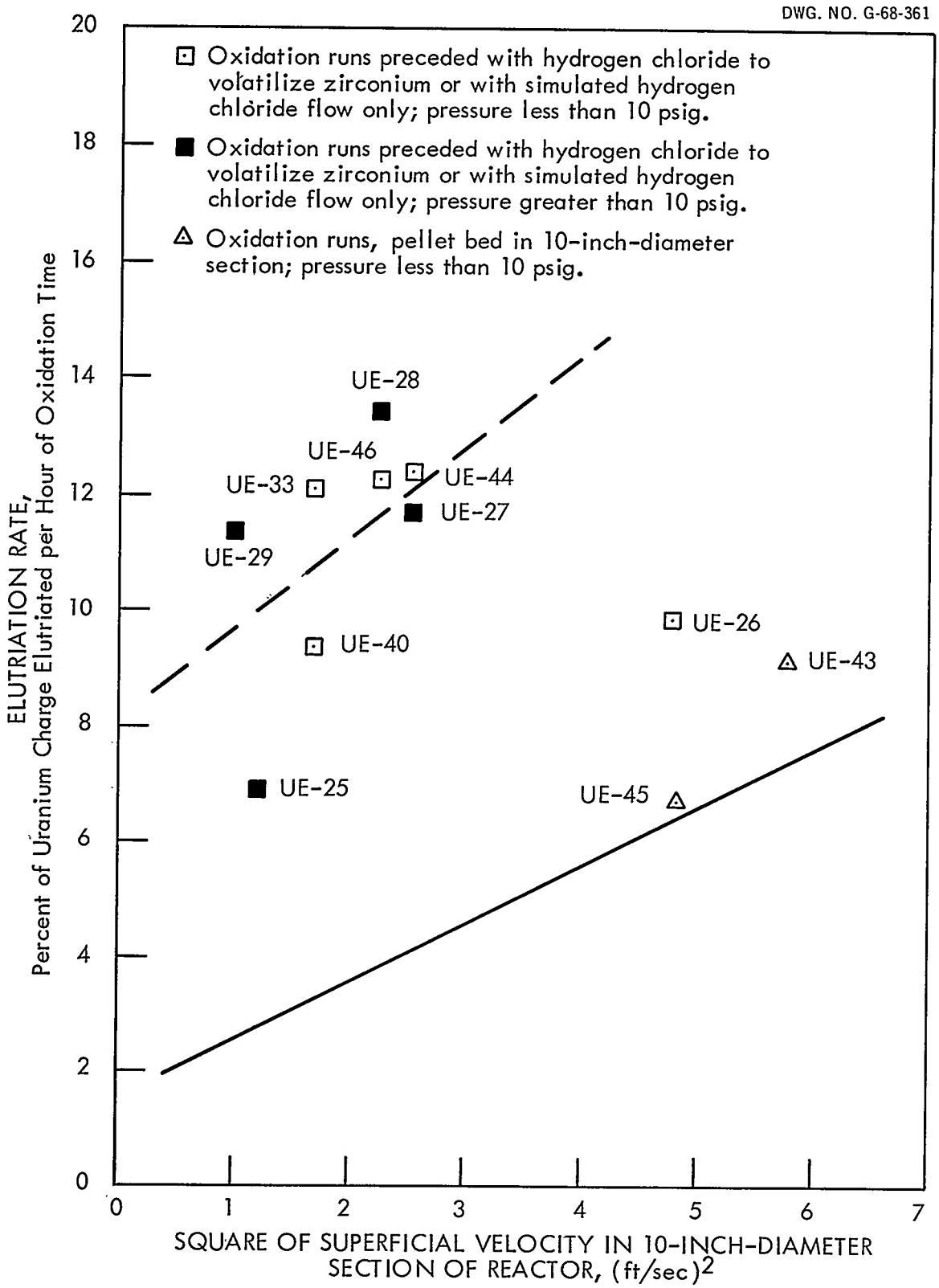
Figure 30

DWG. NO. G-68-542



ZIRCONIUM REACTED AND HCl CONSUMED IN RUN UE-54

Figure 31



ELUTRIATION RATE CORRELATION

Figure 32

published in the report for the previous period*, but new data points, i.e., from runs UE-43 and -45, have been inserted. The results of tests UE-43 and -45, where velocities were about 2.4 and 2.2 ft/sec, respectively, support the original curve. The graphs show the possible association of the elutriation rate with the Froude number and, in addition, make it evident that a higher elutriation rate is achieved after hydrogen chloride treatment. The elutriation rate remained essentially constant over the course of the runs which involved oxidation only. In contrast, the elutriation rates realized during the early part of the oxidation tests which were preceded by a hydrogen chloride treatment decreased if the tailout period was long. Since corrections for long-term tailout could not be readily made, only overall rates were plotted, and consequently, some of the long-run data might be somewhat biased in comparison with the rates from the shorter runs. The plot has not been established statistically but is shown as a broken line to reflect the uncertainties in the data.

The conclusions reached from the results of these tests are as follows:

1. Decladding Tests

   a. A simulated fuel element and a PRTR fuel element were successfully processed through decladding and oxidation in the semiworks reactor.

   b. Results of hydrogen chloride treatment-oxidation tests indicate that the rate of U_3O_8 elutriation is increased after pellet exposures to hydrogen chloride of as little as 1 hour prior to oxidation. These higher rates appear to be of about the same magnitude, regardless of whether the pretreatment consists of exposure to hydrogen chloride or a full zircaloy decladding cycle.

   c. The rate of uranium elutriation during oxidation after decladding the simulated fuel was greater than 10 kg U_3O_8 per 1,000 scf of gas. Since 7 kg of U_3O_8 per 1,000 scf of gas is deemed feasible for a two-vessel plant in which hydrogen chloride decladding is employed, elutriation is probably a practical transfer technique for the two-vessel process.

   d. Hydrogen chloride pretreatment also increases the elutriation selectively for uranium from an alumina-U_3O_8 mixture.

   e. The reaction temperature was controlled satisfactorily during the decladding of the PRTR fuel element. The assistance of the alumina in removing reaction heat during decladding was demonstrated in UE-47. The maximum temperature difference between the center of the fuel element and the fluid bed was only 25°C for the submerged portion of the fuel element during the first 2-3/4 hours

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* K-1744, loc cit, p. 52.

of decladding. On the other hand, the temperature difference at the top of the element, i.e., above the fluid bed, reached a maximum of 61°C. With the breakup of the element, the circulation of the alumina between the rods would improve and better temperature control of the bed would result.

2. Oxidation Tests

a. Although temperature and pressure drop increases are noted during oxidation when uranium dioxide pellets are fed semicontinuously, the effects can be controlled, and bed performance is not upset. In semiworks tests, material was elutriated from the reactor; however, the rate of uranium elutriation was less than the rate at which uranium was charged to the reactor. In a fuel recovery plant, local batching and criticality requirements would make control of fuel material buildup mandatory. Simple bed overflow would be a more reliable means of transferring the uranium in a two-vessel plant; however, it could have the shortcoming of also transferring more alumina than would otherwise be elutriated.

b. A concentration as high as 40% oxygen in nitrogen can be used from the outset of oxidation in shallow pellet beds. No operational problems are expected when 21% oxygen is used. Indications are, based on bed performance in semiworks tests with solid cylindrical pellets, that some periodic vibration might be necessary to control high pressure drop buildup across the beds in plant-scale reactors when 40% oxygen is used. Of course, stepwise buildup to a high oxygen concentration, such as 40%, might be the superior oxidation procedure.

c. Oxidizing EGCR pellets for 3 hours with a feed gas containing 40% oxygen produces a bed of U_3O_8 which appears to be fine enough for fluid-bed fluorination. The final bed obtained under these conditions is similar to that which is obtained with air feed and an oxidation time of 4 to 8 hours.

d. The oxidation of Westinghouse solid cylinder uranium dioxide fuel pellets was conducted without difficulty, and no unusual conditions developed. The same degree of oxidation can be achieved with Westinghouse and annular EGCR pellets.

e. When usual oxidation procedures are used, the comminution of the solid Westinghouse pellets to minus 35-mesh particles is poorer than that obtained with cylindrical EGCR pellets. Some of the smaller lumps are rather soft and might possibly either break up during bed removal and handling or at least might not be stable in the fluidized bed. Others, however, are hard and constitute something of a potential operating problem since good comminution is important in achieving good fluidization, in expediting transfer of fissile material by elutriation, and in preventing sintering during the highly exothermic uranium fluorination step. The

differences observed with solid cylindrical and EGCR pellets might not be so pronounced in an irradiated fuel reprocessing plant, since it is expected that irradiated materials will be more reactive and tend to pulverize more easily because of the cracking and density decreases occurring during irradiation.

f. The rate of uranium elutriation appears to have been improved by about 50% when 40% oxygen was used for oxidation instead of 11 to 21% oxygen.

g. An increase in superficial velocity from 1.5 to 2.4 ft/sec increases the uranium elutriation rate when EGCR pellets are oxidized. Runs UE-41, -42, and -43 were conducted under similar conditions except that the higher velocity was used in the last run. The elutriation rate in UE-43 was approximately twice as great as those of the earlier two runs.

h. The rate of oxidation appears to be doubled when air is used for the entire oxidation cycle instead of using 10.5% oxygen for the first 2 hours and 21% oxygen afterward for final conversion.

i. The cumulative weight of U_3O_8 elutriated during batch runs involving uranium dioxide oxidation at fluidization velocities as high as 2.0 ft/sec increases approximately linearly with time for runs with oxidation cycles up to about 5 hours when the oxidation is not preceded with hydrogen chloride treatment.

j. Most of the alumina elutriation during a batch oxidation generally occurs during the first 2 hours of the run.

k. High semiworks system backpressure does not significantly increase the U_3O_8 elutriation rate from the reactor. This conclusion was made after a comparison of previously obtained high pressure run data with current tests.

Summary of Semiworks Plant Results. The overall reactor system studies from the viewpoint of the ORGDP experimental program might be summarized as follows:

1. Removal of zircaloy cladding by reaction with hydrogen chloride appears to proceed satisfactorily and at sufficient rates for most purposes. Evaluation of the effects of fuel assembly submergence in the fluid bed on chemical declad rate and temperature control indicates that complete submergence of the material in the fluidized bed of alumina is not required. Off-gas filtering remains a problem, with no satisfactory solution of the filter plugging difficulty presently in hand.

2. Oxidation of uranium dioxide pellets can be performed satisfactorily in batch operations with bed depths from several inches to over 3 feet, providing sufficient gas velocity is employed to remove the

formed powdered material from the pellet zone and the reaction zone is localized in the upper few inches or so of the pellet zone. Superficial gas velocities required range from 1 ft/sec in shallow beds to 2.5 to 3.0 ft/sec for the deepest ones tried. Pretreatment of pellets with hydrogen chloride with or without concurrent zircaloy reaction appears to aid comminution and increase elutriation rates in the subsequent oxidation step.

3. Fluorination with elemental fluorine can be performed readily in the fluid bed at temperatures of 350 to 400°C and probably higher. The main difficulty would appear to be elutriation of unreacted material to the filter zone. This probably can be minimized by use of lower gas velocities.

4. Fluorination studies with synthetic beds made by Argonne by processing spiked uranium dioxide through the bromine pentafluoride step indicated that a significant heat release will occur in the elemental fluorine fluorination step due to the failure of bromine pentafluoride to completely convert some of the fission product elements.

   Bromine pentafluoride fluorination was not done in the semiworks. A system for testing this phase of the operation, including regeneration of bromine pentafluoride, collection and separation of uranium hexafluoride and bromine pentafluoride, and recycle of bromine pentafluoride, had been designed and some of the equipment had been built when the close-out order necessitated suspension of this phase of the program.

One limitation of the semiworks test program was the inability to process actual irradiated elements. This part of the program was to have been covered at ORNL in a hot pilot plant which was also cancelled by the program close-out decision. Variability arising from different starting materials and from effects of changes in pretreatment can certainly affect results, as has been indicated to a limited degree in some of the semiworks oxidation tests.

Outlet Gas Filter Studies

Filter permeability losses of 95 to 99% are encountered when sintered nickel filter tubes are subjected to multicycle exposure to hydrogen chloride-stannous chloride-zirconium tetrafluoride-hydrogen-inert gas mixtures typical of the reactor off-gases during the decladding of zircaloy clad power reactor fuels in a fluidized alumina bed. Depending on initial permeability, the maximum tolerable loss for this type of filter in decladding-oxidation-fluorination plant operations is established to be about 90%, if adequate flow in long-term use under exposure to a wide variety of dusts is to be assured.

Since nickel is potentially the most suitable material of construction for a single filter handling the gases from the three-step operation, efforts have been made to determine the plugging mechanism in the hope

that, once the causes were identified, they could be circumvented. Of course, other alternatives might be considered, e.g., separate filters for each process step (thus permitting the use of different materials of construction) or other types of gas cleanup equipment, such as bed filters and cyclones.

Recent tests with the nickel filters have been centered on the volatilization of zirconium tetrachloride from zirconium tetrachloride powder charges to the reactor while the bed was fluidized with hot inert gases. Zirconium tetrachloride sublimate in the gas was thus substituted for declad reaction off-gases, i.e., the hydrogen, hydrogen chloride, and alloy constituents, are eliminated. This technique permits the selective study of the influences of zirconium tetrachloride alone, as well as combinations of zirconium tetrachloride with hydrogen and/or hydrogen chloride. Details of tests with zirconium tetrachloride in argon, and zirconium tetrachloride with argon and hydrogen chloride were given in the previous report*.

During the current test period, nickel filter permeability loss tests were made with hydrogen and with hydrogen and hydrogen chloride in the fluidizing gases, together with the zirconium tetrachloride. In a final test, a sintered powder 316 stainless steel filter was exposed to the off-gases from the declad and oxidation reactions. This material of construction had been proposed for the filtration of reactor off-gases prior to fluorination in a two-reactor process.

A single sintered nickel fiber filter was installed in the test loop in the primary position. The filter loop reactor was then charged with 7.5 kg of minus 48- plus 100-mesh Alcoa tabular alumina and 1.8 kg of zirconium tetrachloride. The bed was fluidized with 70% argon and 30% hydrogen at a superficial gas velocity of 0.75 ft/sec. After the filter had been heated to 315°C, the reactor bed was heated to 425°C at a rate of 50°C per hour, thereby volatilizing the zirconium tetrachloride. To complete a full cycle, the bed was then exposed in succession to air and to 20% fluorine, each at a gas velocity of 1 ft/sec at 480°C for 1 hours. Argon was used as the gaseous diluent. The filter temperature was maintained at 100°C during the oxidation and fluorination. Heated argon blowback of the filter was utilized during all phases of operation.

The reactor was recharged at the start of each cycle. At the completion of ten cycles of operation, the filter appeared to be quite serviceable but was removed for inspection. A very light coating of gray-white powder was noted which analyzed 41.0% zirconium, 12.0% aluminum, 0.41% nickel, 0.16% chloride, and 33.6% fluoride. Flow measurements indicated a 21% permeability loss, which is comparable to the loss experienced when a filter tube is subjected to simulated reaction off-gases without zirconium.

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* K-1744, loc cit.

The filter tube was subsequently reinstalled in the filter loop, the reactor was charged, and the exposure cycling was resumed with hydrochlorination fluidizing gases composed of 50% hydrogen chloride, 30% hydrogen, and 20% argon. After fourteen more cycles of operation, the filter tube was again removed for inspection. The usual filter coating was observed, and the laboratory analyses gave 45.9% zirconium, 6.4% aluminum, 0.66% nickel, 0.12% chloride, and 35.9% fluoride*. X-ray diffraction analysis indicated 70% zirconium tetrafluoride and 30% unknowns. Flow measurements indicated a total permeability loss of 98.7%.

In summary, the results of all the zirconium tetrachloride experiments made with sintered nickel fiber filters are that (1) zirconium tetrachloride plus a mixture consisting of 30% hydrogen and 70% oxygen-free argon resulted in little filter plugging, i.e., about 20% in ten cycles; (2) zirconium tetrachloride and oxygen-free argon gave a 79% permeability loss in ten cycles; and (3) hydrogen chloride, zirconium tetrachloride, and argon, with or without hydrogen, plugged a filter beyond satisfactory use; i.e., in fourteen cycles caused permeability losses of 95% and greater, which are comparable to the plugs experienced with zircaloy-hydrogen chloride reactions. Previous tests with hydrogen chloride and hydrogen, but not zirconium, indicated 25 to 30% permeability losses in nickel fiber filter tubes. It is therefore believed that the difficulty is caused by the presence of both zirconium tetrachloride and hydrogen chloride, and probably involves formation of a complex between these materials and the nickel in the relatively high surface area filter environment. The higher permeability loss with zirconium tetrachloride diluted with argon than with zirconium tetrachloride diluted with both argon and hydrogen is unexplained.

In the exposure test with the 316 stainless steel filter, the test loop was charged with 7.5 kg of minus 48- plus 100-mesh tabular alumina and 0.9 kg of zircaloy tubing. The bed was fluidized for 8 hours with hydrogen chloride in hydrogen and argon† at 400°C and a superficial gas velocity of 0.75 ft/sec, then with air at a velocity of 1 ft/sec and a temperature of 480°C for 10 hours. The filter temperature was maintained during the hydrochlorination and oxidation phases of the cycle at 315 and 100°C, respectively.

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* The major difference between the two filter coating analyses in this report lies in the aluminum content; however, the filter pressure drop does not appear to be affected by the aluminum content. In addition, the aluminum in the coating probably results from elutriation of bed diluent rather than from deposition of a volatile aluminum compound.

† The hydrogen chloride concentration started at 10% and was increased 10% each hour to a maximum of 70% by volume. The hydrogen concentration was held at 30%.

The pressure drop across the filter measured 0.12 psi during the hydrochlorination phase of the first cycle and increased to about 1.5 psi by the sixth cycle. The pressure drop continued to average 1.5 psi during the next thirteen cycles of exposure. Laboratory flow measurements made on the filter tube indicated an initial flow rate of 216 scfm/sq ft-psi pressure drop and a flow rate of 8.5 scfm/sq ft-psi pressure drop at the end of the nineteenth cycle. The permeability loss over the course of the test was 96%. Although this loss appears large, it should be noted that the final flow rate exceeds the 4 scfm/sq ft-psi pressure drop factor used in design calculations for the process gas filters in the conceptual plant.

Samples of a light gray powder coating found on the surface of the tube were sent to the laboratory for analysis. Wet chemistry analyses indicated the presence of 29.08% zirconium, 17.26% aluminum, 8.84% nickel, 12.81% chloride, and 91.3% fluoride. The nickel analysis is higher than that found in most of the previous tests; this magnitude may be attributable to the corrosive action of the hydrogen chloride on the stainless steel material of construction. The material also analyzed semiquantitatively, by X-ray diffraction, at about 60% zirconium dioxide, 20% alumina, and 20% unknown. The diffraction patterns exhibited by this unknown component are similar to the patterns for the unknown component in the coatings on nickel fiber filters in past tests. It was therefore concluded that the plugging mechanism may be similar to that for sintered nickel tubes.

The filter tube for general use with volatility process off-gases has obviously yet to be found. Separate filters for decladding and fluorination might, in the long run, prove to be most practical from the corrosion standpoint. There would probably be no problems with the use of nickel filters for fluorination off-gases, and stainless steel should be suitable chemical decladding. There are no foreseen difficulties with either of these materials in filtering off-gases from the oxidation step.

Product Purification Sorption-Desorption Tests

In volatility operations, uranium hexafluoride sorption on sodium fluoride can be effectively employed for uranium product purification and recovery, as well as the decontamination of process exhaust streams. The sorption has been demonstrated in ORGDP tests with gas streams containing from 130 ppm to 10% uranium hexafluoride. A trap 4 inches in diameter was used, 120°C was chosen as the operating temperature, and gas velocities ranged from 0.08 to 1 ft/sec. The sorbed uranium hexafluoride was removed by heating and collected in a relatively pure form, leaving the

sodium fluoride regenerated for future use. The results have been published in previous progress reports*.

In the tests with low concentrations of uranium hexafluoride, a velocity of 0.7 ft/sec was employed. During the current report period, two new studies were made to cover higher gas flow, low uranium hexafluoride concentration cases, such as might be encountered with exhaust gases from a cold trap backup system to a sorption system in the event of a dilute gas release. The sorbent material was prepared by heating 1/8 inch cylindrical commercial sodium bifluoride pellets at 538°C for 5 hours. The resultant sodium fluoride had a surface area of 1.44 sq m/g, a void fraction within the pellet of 0.505, and a pellet density of 1.43 g/cc. For each test, approximately 18 kg of the sodium fluoride pellets was charged to the 4-inch-diameter trap to form a 7-foot-deep bed, and a superficial gas velocity of 1 ft/sec was employed. The gas flowed through the trap in the downward direction.

The first run lasted 1,820 hours. The operating temperature was 120°C, and the uranium hexafluoride concentration in the inlet stream was maintained at about 120 ppm. Although breakthrough did not occur during the test, the uranium hexafluoride analyses of the outlet gas stream averaged 30 ppm. This concentration was higher than expected. Pellet descriptions and analyses of uranium content at the conclusion of the test are given in table XX as a function of bed location.

A study of the test temperature data indicated that the middle section of the trap averaged about 4 to 6°C higher than at the ends. The uranium content of the pellets was lowest in this area of the bed, and it is possible that sorption was poor there because of the higher temperature. Reduction of test temperature is suggested as a possible means of improving sorption efficiency. The 120°C condition was chosen as a condition that would minimize hydrogen fluoride sorption in the event significant quantities were present. Sufficient hydrogen fluoride rejection might be achieved at slightly lower temperatures. On the other hand, selective regeneration may be possible so that the hydrogen fluoride and uranium hexafluoride may be separated in spite of the sorption of both on the sodium fluoride.

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* Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies, Summary Progress Report, Fiscal Year 1964 through Fiscal Year 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, October 29, 1965 (K-1649), pp. 74 to 80; Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies, Summary Progress Report, July through December, 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, June 28, 1965 (K-1669), pp. 48 and 49; K-1691, loc cit, p. 57; K-1738, loc cit, pp. 83 to 85; and K-1744, loc cit, pp. 61 and 62.

TABLE XX

SODIUM FLUORIDE PELLET SORPTION DATA
AFTER 1,820-HOUR RUN AT 120°C*

Pellet Location in Bed	Uranium Concentration, %	Color of Pellet
Top	25.0	Dark yellow
6 Inches from Top	25.0	Dark yellow
1 Foot from Top	24.7	Dark yellow
1-1/2 Feet from Top	22.1	Dark yellow
2 Feet from Top	21.0	Dark yellow
2-1/2 Feet from Top	6.3	Light yellow
3 Feet from Top	2.9	White
3-1/2 Feet from Top	2.7	White
4 Feet from Top	1.8	White
4-1/2 Feet from Top	2.6	White
5 Feet from Top	2.4	White
5-1/2 Feet from Top	3.3	Light yellow
6 Feet from Top	4.6	Light yellow
6-1/2 Feet from Top	7.1	Light yellow

* The inlet uranium hexafluoride concentration was about 120 ppm, the sodium fluoride bed was 7 feet high, and the nominal residence time was 7 seconds.

The second run consisted of a series of tests at temperatures between 66 and 135°C to determine the effect of temperature on the outlet concentration of uranium hexafluoride. The inlet uranium hexafluoride concentration was adjusted for a target value of about 200 ppm and the resultant uranium hexafluoride concentrations in the outlet gas were determined.

The results, shown in table XXI and plotted in figure 33, indicate that an operating temperature of 93 ± 8°C should be satisfactory and would result in an exit gas containing about 4 ppm uranium hexafluoride. As shown in the data, even though the bed temperature was reduced to 66°C, outlet concentrations of greater than 1 ppm were observed. It may be that these last results are biased high because the trap used has seen long-term uranium hexafluoride service, and some uranium hexafluoride background may exist throughout the system.

The observed uranium hexafluoride concentrations were compared with computed gas concentrations based on equilibrium pressure equations from ORNL-2661* and ORNL-3497† for uranium hexafluoride over the $UF_6 \cdot 2NaF$ complex. Extrapolation down to test temperatures was necessary, since the reference data were obtained at much higher temperatures. The uranium hexafluoride concentrations observed in this run fell between the values obtained from the two references.

It seems that outlet concentrations close to equilibrium are being achieved with the nominal 7-second residence time. Thus, use of a deeper bed or lower gas flow rate would probably not result in significant reduction of the outlet concentration.

PERIPHERAL COMPRESSOR

After 3,813 hours of operating, including 2,340 hours of pumping mixtures of gas containing small amounts of uranium hexafluoride and fluorine, the compressor was shut down to inspect and replace the bearings. In the 54 hours of operation prior to shutdown, the load bearing temperature had increased from 54 to 79°C. One cubic centimeter of oil was injected into the bearing area, but there was no substantial decrease in temperature.

The unit had been in service on the second set of bearings since January, 1967, and had required no maintenance. Over the report period until shutdown, the compressor was operated at 9,500 rpm, the suction and

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* Cathers, G. I., Bennett, M. R., and Jolley, R. L., The Fused Salt-Fluoride Volatility Process for Recovering Uranium, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, April 1, 1959 (ORNL-2661).

† Katz, S., Apparatus for the Gasometric Study of Solid-Gas Reactions: Sodium Fluoride with Hydrogen Fluoride and Uranium Hexafluoride, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, October 29, 1963 (ORNL-3497).

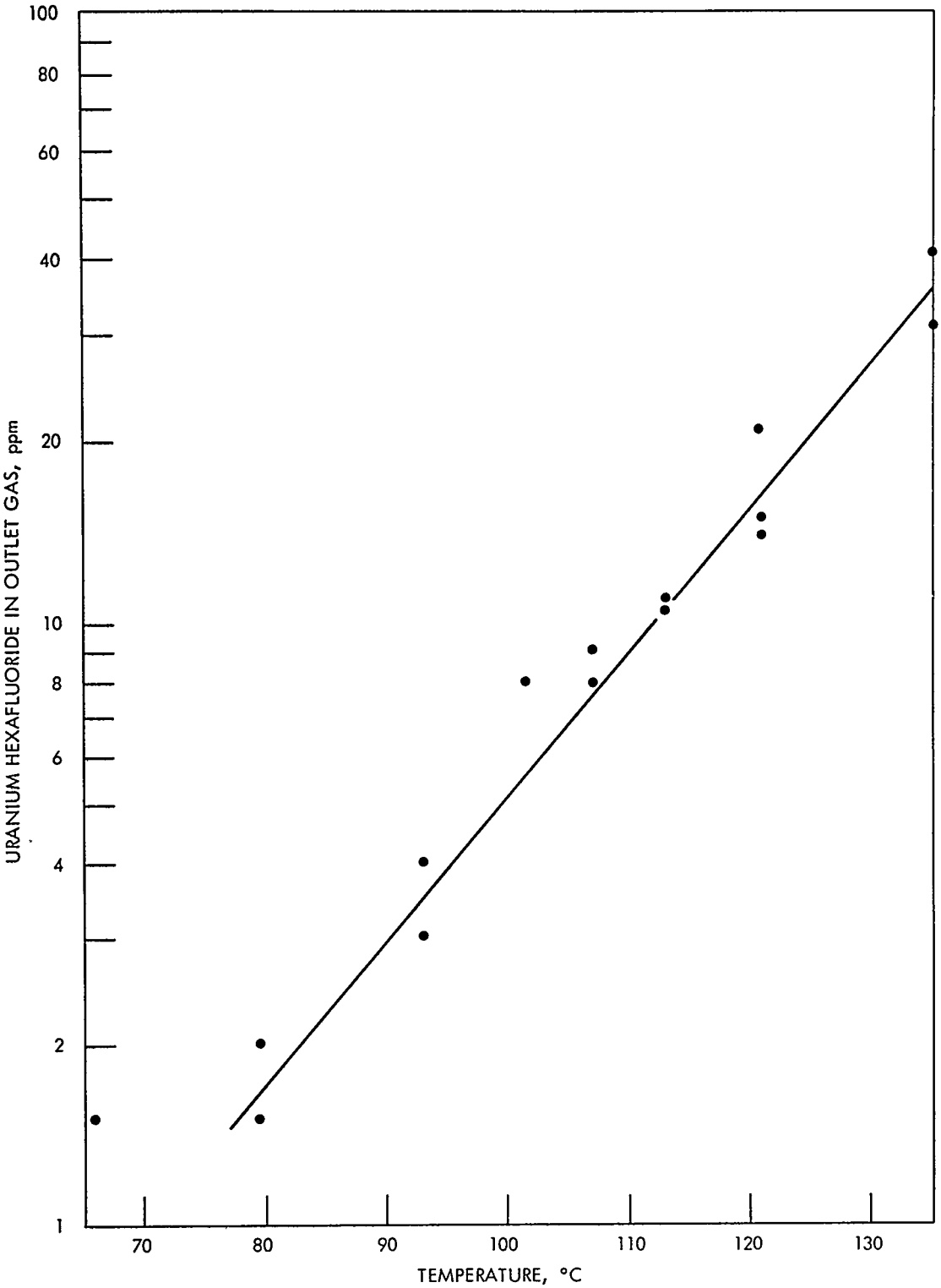
TABLE XXI

SODIUM FLUORIDE PELLET SORPTION DATA
AT TEMPERATURES FROM 66 TO 135°C*

Temperature, °C	Uranium Hexafluoride Inlet Concentration, ppm	Uranium Hexafluoride Outlet Concentration, ppm
66	180	1.5
66	177	1.5
80	156	2
80	172	1.5
93	182	4
93	176	3
102	233	8
107	232	8
107	115	9
113	178	11
113	180	12
121	312	14
121	345	15
121	274	21
135	330	31
135	347	41

* Inlet uranium hexafluoride concentration was approximately 200 ppm, the sodium fluoride bed was 7 feet high, and the nominal residence time was 7 seconds.

DWG. NO. G-68-418



URANIUM HEXAFLUORIDE CONCENTRATION IN OUTLET GAS AS A FUNCTION OF SORPTION TRAP TEMPERATURE

Figure 33

discharge pressures were 12 and 28 psia, respectively; the corresponding power requirement was 5.75 kw, and the load and rear bearing temperatures had been 54 and 43°C.

The compressor was removed from the test loop and was disassembled. Unusual difficulty was encountered in disassembling the process side with the cover plate and the impeller especially hard to remove. All surfaces which had been in contact with the process were covered by an adhering layer of uranium salts, principally uranyl fluoride. This type of deposit is not unusual for equipment used in uranium hexafluoride service. There had been no dusting. The metal surfaces coming into contact with the corrosive gases were easily cleaned with water, and inspection showed no signs of attack.

The general condition of the rear bearing was excellent. The grease that was packed throughout the bearing, although slightly stiff, appeared to possess much of its initial lubricity. The balls, phenolic retainer, and bearing races looked especially clean.

Inspection of the load bearing assembly showed that the bearing set nearest the compressor motor was responsible for the overheating. The forward bearing set was deficient in the amount of grease packed around the balls, but was not dry. The oil injected into the bearing area just before shutdown had obviously reached this point. The second bearing set, on the other hand, contained grease but was very dry. The phenolic retainer was found to have been broken at one place. The surfaces of the inner and outer races on which the balls ride were found to be moderately damaged. All of the balls of the second bearing set were slightly marred, with one ball being galled. The evidence classified the bearing failure as a normal one, resulting from degradation of the lubricating qualities of the bearing grease through routine use.

The grease-lubricated bearings performed well beyond the expected life of 2,500 hours. The compressor was designed for remote maintenance in an operating cell. The grease system was chosen over more conventional recirculating oil lubrication for design simplicity and for ease of removal of the entire compressor from a remote location, such as a processing cell, for maintenance purposes. In more conventional applications, an oil system would probably have been used.

The compressor was reassembled, with all new bearings, and was returned to service for 586 additional hours prior to conclusion of the long-term durability tests. Throughout this final test period, operation was again normal, and there were no unscheduled shutdowns.

It has been concluded as the result of these tests that the compressor is potentially suited for the recycle of reagent gases in volatility process applications. Test performance with mixtures of fluorine has exceeded the design criteria, and the long-term durability test program has demonstrated the mechanical reliability of the unit.

A formal report will soon be published which will give detailed information on the entire development and testing program. An analysis of the results of tests comparing design performance curves with actual performance data will be included.